salts of 2-methyl-1-naphthaldehyde tosylhydrazone and identified by its mass spectrum (*m/e* 154 (M)) and comparison of its rather structured uv with that of the known material.[67]

2-Methyl-4,5-benzotropone Tosylhydrazone. In a typical run, 2.00 g (0.012 mol) of 2-methyl-4,5-benzotropone, 2.18 g (0.012 mol) of *p*-toluenesulfonylhydrazide, and 5 drops of concentrated sulfuric acid were placed in 40 ml of absolute ethyl alcohol and heated at reflux for 1 hr. Upon cooling, 2-methyl-4,5-benzotropone tosylhydrazone precipitated from solution and was isolated by filtration. Recrystallization from absolute ethyl alcohol yielded 2.4 g (60%) of the product as yellow-gold plates, mp 182–184°: ir (KBr) 3180, 1630, 1590, 1555, 1420, 1385, 1330, 1165, 1022, 915, 805, 760, 680, and 580 cm^{-1}; nmr ($CDCl_3$) τ 2.00–3.00 (A_2B_2, 4 H, J = 8 cps, aromatic), 2.78 (s, 4 H, benzo), 3.05–3.70 (m, 3 H, cycloheptatrienyl), 7.62 (s, 3 H, *p*-methyl), 7.88 (d, 3 H, cycloheptatrienyl methyl); mass spectrum 339 (M^+). *Anal.* Calcd for $C_{19}H_{18}N_2O_2S$: C, 67.43; H, 5.36; N, 8.28. Found: C, 67.39; H, 5.33; N, 8.40.

Pyrolysis of the Sodium Salt of 2-Methyl-4,5-benzotropone Tosylhydrazone in Benzene. To a Fischer–Porter aerosol compatibility tube containing 35 ml of benzene was added 216 mg (0.60 mmol) of the sodium salt of 2-methyl-4,5-benzotropone tosylhydrazone. The sealed tube was placed in an oil bath preheated to 130° for 20 min. By the end of this time the yellow mixture had changed to a very light yellow-green. The mixture was allowed to cool and filtered. The residue was washed with ethyl ether and the total filtrate concentrated on a rotary evaporator to yield 80 mg of products. Analysis of the product mixture by nmr indicated the presence of 2-vinylnaphthalene and 2-(2,4,6-cycloheptatrien-1-yl)-3-methylnaphthalene (comparisons were made using commercially available 2-vinylnaphthalene from Aldrich Chemical Co. and 2-(2,4,6-cycloheptatrien-1-yl)-3-methylnaphthalene from the pyrolysis of the sodium salt of the tosylhydrazone of 2-methyl-3-naphthaldehyde in benzene). Analysis by vpc (3 ft × 0.25 in. 15% SE-30 on Chromosorb W at 190°) indicated three products in the reaction mixture (the known ones were established by comparison with known samples): (1) retention time 1 min, 2-vinylnaphthalene (72%); (2) retention time 10 min, unknown compound (6%); (3) retention time 14 min, 2-(2,4,6-cycloheptatrien-1-yl)-3-methylnaphthalene (22%). Products 1 and 3 were isolated in 44% and 20% overall yield, respectively. 2-(2,4,6-Cycloheptatrien-1-yl)-3-methylnaphthalene (sublimed at 90° and 0.1 mm) had the following properties: mp 65–68°; ir (KBr) 3055, 3010, 1600, 1500, 1440, 1220, 1010, 890, 745, 700, and 480 cm^{-1}; nmr ($CDCl_3$) τ 2.00–2.90 (m, 6 H, naphthyl), 3.25 (broad s, 2 H, 4 and 5 cycloheptatrienyl), 3.50–3.90 (complex pattern, 2 H, 3 and 6 cycloheptatrienyl), 4.35–4.76 (complex pattern, 2 H, 2 and 7 cycloheptatrienyl), 6.95 (broad t, 1 H, methine), 7.65 (s, 3 H, methyl); mass spectrum 232 (M^+). *Anal.* Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 92.85; H, 7.00.

The sodium salt of 3-methyl-2-naphthaldehyde tosylhydrazone was pyrolyzed in the same manner as the above salt except that 40 ml of benzene was used and the temperature was 145°. The products were aldazine (42%) and 2-(2,4,6-cycloheptatrien-1-yl)-3-methylnaphthalene (39%).

Acknowledgment. The authors are indebted to the National Science Foundation and to the Petroleum Research Fund, administered by the American Chemical Society, for their generous support of this research.

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(67) M. P. Cava, R. L. Shirley, and B. W. Erickson, *J. Org. Chem.*, 27, 755 (1962).

Recovery of *R* Allenes from the Partial Hydroboration of Racemic Allenes with (+)-Tetra-3-pinanyldiborane. A Model for Hydroboration of Olefins and Allenes[1]

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Abstract: A series of racemic allenes was partially hydroborated with (+)-tetra-3-pinanyldiborane derived from (−)-α-pinene. In every case the recovered allene was enriched in the *R* enantiomer. Where necessary, absolute configurations were assigned by reference to allene sector rules in conjunction with ORD–CD measurements. Optical purities appeared to increase in the order 1,3-dimethylallene < 1,2-cyclononadiene < 1,3-di-*tert*-butylallene < 1,3-diethylallene < 1,3-di-*n*-propylallene. Hydroboration of both 1,3-di-*tert*-butylallene and 1,3-diethylallene with both fresh and aged tri- and di-3-pinanyldiborane reagents gave recovered allene having a lower optical purity but still the *R* configuration. The regiospecificity, *ca.* 70% vinyl- and 30% allylborane formation (determined for 1,2-cyclononadiene), paralleled that found previously for other reagents. An analysis of prior data and models for hydroboration of olefins has led to the proposal of a model for asymmetric hydroboration with tetra-3-pinanyldiborane. This model, which uses a simple shape for the reagent and allows nonplanarity of a four-center transition state, correctly predicts the stereochemistry of hydroboration of allenes.

Over a decade ago, Brown and his coworkers introduced the use of optically active alkylboranes as hydroborating agents which could effect the transformation of an appropriate olefin into an optically active alcohol.[2] At the same time, Brown showed that from the partial hydroboration of a chiral olefin it was possible to achieve a "kinetic resolution" leading to the recovery of an optically active olefin.[2b,3] To date, the most useful reagent has proved to be the first one reported by Brown, *viz.*, tetra-3-pinanyldiborane, hereafter referred to as $Pn_4B_2H_2$ or $Pn_2BH_2BPn_2$.[4]

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(1) Acknowledgment is made to the National Science Foundation for support of this research (GP 25216).

(2) (a) H. C. Brown and G. Zweifel, *J. Amer. Chem. Soc.*, 83, 486 (1961); (b) H. C. Brown, N. R. Ayyangar, and G. Zweifel, *ibid.*, 86, 397 (1964).

(3) H. C. Brown, N. Ayyangar, and G. Zweifel, *ibid.*, 86, 4341 (1964).

(4) The *Chemical Abstracts* name for this reagent is tetra-3-pinanyldiborane although it commonly has been referred to as tetraisopinocampheyldiborane. Similarly di-3-pinanylborane has been called diisopinocampheylborane. We will follow the recommendation[5] that the less cumbersome *Chemical Abstracts* nomenclature be used.

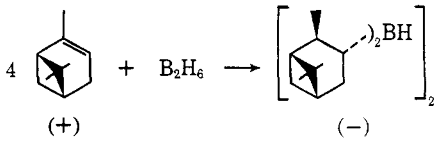
(5) J. D. Morrison and H. S. Mosher, "Asymmetric Organic Reactions," Prentice-Hall, Englewood Cliffs, N. J., 1971, p 220 ff.

Table I. Partial Hydroboration of 1,3-Dialkylallenes with Tetra-3-pinanyldiborane

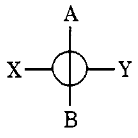
Allene	Reagent[a]	Solvent[b]	Time,[c] min	Reduction, %	Recovered allene $[\alpha]^{22}_{578}$,[d] deg	$[\phi]^{22}_{578}$,[d] deg
1,3-Dimethyl	$Pn_4B_2H_2$[e]	DEC	5	67	−22.7[f]	−15.4
1,3-Dimethyl	$Pn_4B_2H_2$[e]	DEC	5	67	−21.5[f]	−14.6
1,3-Diethyl	$Pn_4B_2H_2$[e]	DEC	20	67	−57.6	−55.3
1,3-Diethyl	$Pn_4B_2H_2$[g]	DG	20	67	−56.5	−54.2
1,3-Di-*n*-propyl	$Pn_4B_2H_2$[g]	DG	80	67	−51.7	−64.2
1,3-Di-*n*-propyl	$Pn_4B_2H_2$[g]	DG	80	67	−50.0	−62.1
1,3-Di-*tert*-butyl	$Pn_4B_2H_2$[e]	DEC	1440	67	−18.2	−27.7
1,2-Cyclononadiene	$Pn_4B_2H_2$[e]	DG	5	67	+27.4[h]	+33.4

[a] 0.33 mol of $Pn_4B_2H_2$ used per mol of allene. [b] DEC = diethylcarbitol, DG = diglyme. [c] Time required for completion of reaction. [d] Measured in pentane or heptane, *c* 0.3–1.3. [e] Prepared from α-pinene with $[\alpha]^{22}\text{D}$ −51.4° (*c* 8.3, $CHCl_3$). [f] Caserio, *et al.*,[7] reported obtaining $[\alpha]\text{D}$ −17.1 to −43.8° (ether), for *ca.* 50% reduction. [g] Prepared from α-pinene with $[\alpha]^{22}\text{D}$ −48.5° (*c* 8.4, $CHCl_3$). [h] Caserio, *et al.*,[14] reported obtaining $[\alpha]^{23}\text{D}$ +26.5° (neat) for *ca.* 50% reduction.

This reagent is readily made by the combination of 4 mol of α-pinene with 1 mol of diborane. Employing (+)-α-pinene, one obtains (−)-$Pn_4B_2H_2$. Brown established that this reagent exists as the diborane derivative rather than as a monomer,[6] although it often is referred to in the latter sense. This optically active reagent has proved to be extremely useful in asymmetric syntheses and many applications have been recorded.[5]



In seeking a route to optically active allenes, which in general are not readily available, Caserio and her coworkers applied Brown's reagent to 1,3-dimethylallene and 1,3-diphenylallene and found that partial hydroboration led to allene of moderate activity.[7] In both cases, the use of (+)-$Pn_4B_2H_2$ gave recovered (−)-allene. Fortunately, it was possible to determine the stereochemical course of the reaction. Based on a coupled oscillator model, Mason and Vane[8] had previously assigned the *R* configuration to (−)-1,3-diphenylallene. Lowe,[9] utilizing this assignment along with several others, extended Brewster's[10] original helical model of optical activity to allenes and proposed a rule for assigning the absolute configuration of an allene based on its rotation at the sodium D line and the relative polarizabilities of the substituents. Brewster has subsequently amplified[11] his original model and has developed similar predictions in a more detailed way. While the Lowe–Brewster model is really empirical, it has general applicability provided that certain restrictions are met.[12] Recently Mason and coworkers have developed a more general model of optical activity for allenes which, among other things, delineates the basis and validity of the Lowe–Brewster rule.[13]



relative polarizability	sign of rotation at the D line
A > B, X > Y	(−)
A > B, Y > X	(+)

Applying Lowe's rule to 1,3-dimethylallene leads to assignment of the *R* configuration to the (−) enantiomer. Thus Caserio and her coworkers concluded that in both of the cases which they had examined the partial asymmetric hydroboration led to recovery of allene enriched in the *R* enantiomers.[7] However the authors considered that the complexities of hydroboration precluded any mechanistic interpretation.[7b]

In connection with other studies, we have used this reaction as a convenient source of optically active allenes in systems where the stereochemistry can be defined. It appeared to us that although hydroboration is indeed complex, a reasonable mechanistic rationale should be attainable.

Results

Selectivity. 1,3-Dimethylallene, 1,3-diethylallene, 1,3-dipropylallene, 1,3-di-*tert*-butylallene, and 1,2-cyclononadiene were hydroborated with $Pn_4B_2H_2$. The dimethyl case was repeated both as a control for us as well as to provide the optically active allene for optical rotatory dispersion (ORD) and circular dichroism (CD) measurements. Subsequent to completion of our experiments, Byrd and Caserio[14] have reported the partial hydroboration of 1,2-cyclononadiene. Although the series of compounds we have examined is not large, it does provide representative examples of 1,3-dialkylallenes having different structural features. Of equal importance at this stage, we can provide unequivocal arguments defining the stereochemical outcome.

Since, as we note later, a question of the nature and composition of the hydroborating agent can arise depending upon how it is prepared, we followed the original procedures of Brown for preparing $Pn_4B_2H_2$ (and $Pn_3B_2H_3$) at 0°. Both diglyme (diethylene glycol dimethyl ether) and diethylcarbitol (diethylene glycol diethyl ether) have been used as solvents with no difference in the outcome. Partial hydroborations were carried to two-thirds completion to give somewhat higher rotations, improving the signal to noise ratio in

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(6) H. C. Brown and G. J. Klender, *Inorg. Chem.*, **1**, 204 (1962).

(7) (a) W. L. Waters and M. C. Caserio, *Tetrahedron Lett.*, 5233 (1968); (b) W. L. Waters, W. S. Linn, and M. C. Caserio, *J. Amer. Chem. Soc.*, **90**, 6741 (1698).

(8) S. F. Mason and G. W. Vane, *Tetrahedron Lett.*, 1593 (1965).

(9) G. Lowe, *Chem. Commun.*, 411 (1965).

(10) J. H. Brewster, *J. Amer. Chem. Soc.*, **81**, 5475 (1959).

(11) J. H. Brewster, *Top. Stereochem.*, **2**, 33 (1967).

(12) W. R. Moore, H. W. Anderson, S. D. Clark, and T. M. Ozretich, *J. Amer. Chem. Soc.*, **93**, 4932 (1971).

(13) P. Crabbé, E. Velarde, H. W. Anderson, S. D. Clark, W. R. Moore, A. F. Drake, and S. F. Mason, *Chem. Commun.*, 1261 (1971).

(14) L. R. Byrd and M. C. Caserio, *J. Amer. Chem. Soc.*, **93**, 5758 (1971).

Table II. Partial Hydroboration of 1,3-Dialkylallenes with Di- and Tri-3-pinanyldiborane

Allene	Reagent (mol)[a]	Solvent[b]	Time,[c] min	Reduction, %	Recovered allene $[\alpha]^{22}{}_{578}$,[d] deg
1,3-Diethyl	$Pn_3B_2H_3$ (0.67)	DG	5.5	55	−28.5
1,3-Diethyl	$Pn_3B_2H_3$ (0.67), aged[e]	DG	8	82	−52.7
1,3-Diethyl	$Pn_2B_2H_4$ (0.33)	DG	4.8	56	−10.2
1,3-Diethyl	$Pn_2B_2H_4$ (0.33)[f]	DEC	5	64	−15.5
1,3-Diethyl	$Pn_2B_2H_4$ (0.33), aged[e]	DG	5.5	75	−20.9
1,3-Di-*tert*-butyl	$Pn_3B_2H_3$ (0.67)	DG	330	72	−8.0
1,3-Di-*tert*-butyl	$Pn_2B_2H_4$ (0.33)	DG	225	68	−9.6
1,3-Di-*tert*-butyl	$Pn_2B_2H_4$ (0.33)[f]	DEC	360	67	−7.8

[a] Prepared from α-pinene with $[\alpha]^{22}D$ −48.5° (*c* 8.4, $CHCl_3$) except as noted. [b] DG = diglyme, DEC = diethylcarbitol. [c] Time at which the reaction was stopped. [d] Measured in pentane or heptane, *c* 0.5–0.8. [e] Reagent stirred overnight at 22° before use. [f] Prepared from α-pinene with $[\alpha]^{22}D$ −51.4° (*c* 8.3, $CHCl_3$).

the far-ultraviolet in subsequent ORD and CD measurements. The reactions were monitored by removing samples for subsequent glc analysis in order to determine how much time was required for the hydroboration to reach completion (all $Pn_4B_2H_2$ consumed). The results of these runs are summarized in Table I. Both 1,3-dimethylallene and 1,2-cyclononadiene were hydroborated very rapidly—the reactions were complete within 5 min! Because of this rapidity it is essential to add the allene "instantly" to the $Pn_4B_2H_2$ to ensure that enantiomeric competition is always maintained. On large-scale preparative runs it would be wise to reverse the addition to ensure that the allene is always present in excess or else selectivity will be lost. Hydroboration of 1,3-diethylallene was slower and 1,3-dipropylallene reacted still more slowly. However both were much more reactive than 1,3-di-*tert*-butylallene which required *ca.* 24 hr for complete hydroboration. Employing (+)-$Pn_4B_2H_2$ (from (−)-α-pinene), all of the acyclic allenes afforded the (−) enantiomers while 1,2-cyclononadiene gave the (+) enantiomer.

Since 1,3-di-*tert*-butylallene reacted so slowly, it appeared possible that $Pn_4B_2H_2$ was not the hydroborating agent. Brown has shown that $Pn_4B_2H_2$ is in equilibrium with $Pn_3B_2H_3$ and α-pinene, dissociation being *ca.* 6% in diglyme at 0°.[6] With olefins which react slowly, *e.g.*

$$Pn_2BH_2BPn_2 \rightleftharpoons Pn_2BH_2BPnH + \alpha\text{-pinene}$$

hindered cis olefins and trans olefins, the less hindered $Pn_3B_2H_3$, continuously replenished by the slow dissociation, appears to be the actual hydroborating agent.[15] In the present case, α-pinene was observed upon analysis of the reaction mixtures obtained upon hydroboration of 1,3-di-*tert*-butylallene (in the case of the other allenes, small amounts of α-pinene were observed in the glc analyses). This result indicates that the reaction followed the "hindered olefin" path, although it is possible that the α-pinene was eliminated from the hindered trialkylborane obtained if normal addition occurred.

To clarify the nature of the hydroborating agent, "pinene deficient" reagents were examined. With preformed $Pn_3B_2H_3$ prepared from (−)-α-pinene, 1,3-di-*tert*-butylallene was reduced more rapidly, albeit still rather slowly. Again (−)-allene was recovered, although the rotation was only about half that obtained when $Pn_4B_2H_2$ was used (Table II). To examine the effect of still less hindered reagents, $Pn_2B_2H_4$ was prepared from 2 mol of (−)-α-pinene per mole of diborane. With this reagent, 1,3-di-*tert*-butylallene was partially hydroborated to give recovered (−)-allene having about the same rotation as was obtained with $Pn_3B_2H_3$ (Table II). While the less hindered reagents led to reduced optical purities, the (−)-allene was always obtained.

We then examined the behavior of an unhindered allene, 1,3-diethylallene, with the di- and tri-3-pinanyldiborane reagents (Table II). In this case the rapidity of the reaction caused difficulties in controlling the extent of hydroboration. When employing the $Pn_3B_2H_3$ and $Pn_2B_2H_4$ we based the stoichiometry on hydroboration with the nonbridging hydrogens and aimed at reaction of two-thirds of the allene. However the diborane derivatives formed upon addition of the pinene-deficient reagents to an allene are still hydroborating agents. At least in the case of diethylallene they obviously are quite reactive. Since glc monitoring could only give after-the-fact information, we guessed at reaction times. As a consequence the extent of reduction varied from the goal of two-thirds. Nonetheless, the data are sufficient to establish the trends. The rotation of the recovered allene dropped considerably on going from the $Pn_4B_2H_2$ to the $Pn_3B_2H_3$ to the $Pn_2B_2H_4$ reagent. But again, the sign of the rotation was unchanged, (−)-α-pinene led to (−)-allene.

In these experiments with $Pn_3B_2H_3$ and $Pn_2B_2H_4$, both were used as "fresh" reagents, *i.e.*, immediately after being prepared. In view of the fact that Giddings and Mislow[16] had found that "aging" $Pn_2B_2H_4$ can lead to anomalous results (aged reagents led to hydroboration in the opposite stereochemical sense) it seemed wise to investigate this variable. Aged $Pn_3B_2H_3$ gave a much larger rotation for recovered 1,3-diethylallene than was obtained with the fresh reagent (the extent of reaction was greater too causing part of the increase in rotation). The increased rotation indicates that the freshly-prepared reagent must consist chiefly of a mixture of $Pn_4B_2H_2$ and $Pn_2B_2H_4$. Hydroboration thus occurs largely, if not exclusively, with the less selective $Pn_2B_2H_4$. Aging shifts the composition to predominantly $Pn_3B_2H_3$ ($Pn_4B_2H_2 + Pn_2B_2H_4 \rightleftharpoons 2Pn_3B_2H_3$). Based on Brown's results with other alkyldiboranes,[6,17] the postulate that the initially formed reagent would tend to consist of a mixture of $Pn_4B_2H_2$ and $Pn_2B_2H_2$ appears to be reasonable.

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(15) H. C. Brown, N. R. Ayyangar, and G. Zweifel, *J. Amer. Chem. Soc.*, **86**, 1071 (1964).

(16) (a) D. J. Sandman, K. Mislow, W. P. Giddings, J. Dirlam, and G. C. Hanson, *ibid.*, **90**, 4877 (1968); (b) W. P. Giddings and J. Dirlam, *ibid.*, **85**, 3900 (1963).

(17) H. C. Brown, A. Tsukamoto, and D. B. Bigley, *ibid.*, **82**, 4703 (1960).

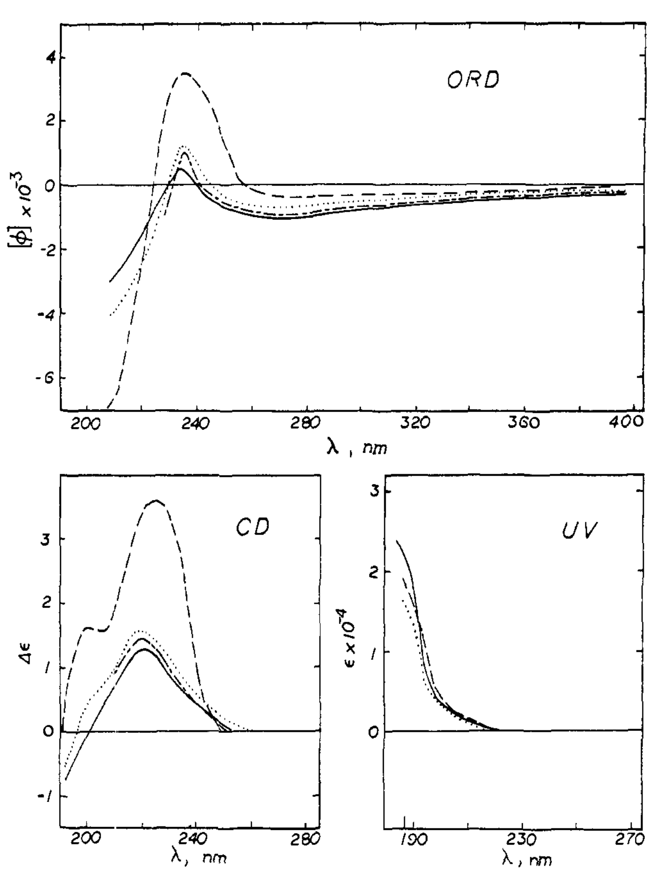
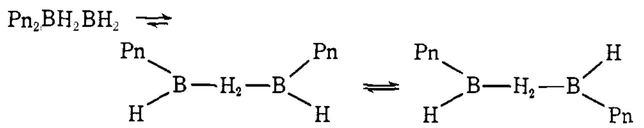


Figure 1. ORD, CD, and uv spectra of acyclic allenes: (– – –) (−)-1,3-dimethylallene; (· · ·) (−)-1,3-diethylallene; (— — — –) (−)-di-*n*-propylallene; (——) (−)-1,3-di-*tert*-butylallene. In order to provide a basis for comparison, the optically pure allenes were arbitrarily assumed to have $[\alpha]_D$ −100°.

Similarly, aging $Pn_2B_2H_4$ led to recovered 1,3-diethylallene with a rotation *ca.* twice that obtained with the fresh reagent. In this case, the initial reagent must have been a complex mixture of the tetra-, tri-, di-, and mono-3-pinanyldiboranes, with reduction resulting from the more reactive, less substituted diboranes. Aging would shift the composition toward $Pn_2B_2H_4$, probably in the sense favoring the symmetrical cis and trans isomers which should be somewhat more selective than the unsymmetrical derivative.



In view of the aging results, it appears probable that the actual reducing agent in hydroboration of di-*tert*-butylallene with $Pn_4B_2H_2$ was mainly $Pn_3B_2H_3$.

Although the composition of the reagent is open to question when reagents less substituted than $Pn_4B_2H_2$ are prepared and hydroborations with such pinene-deficient reagents are less selective than with $Pn_4B_2H_2$, the most important fact that emerges is that *with all of these reagents, pinene deficient or not, the sense of the asymmetric reduction stays the same.* Obviously to prepare allenes with the highest possible rotations, $Pn_4B_2H_2$ should always be used.

Allene Configurations. As we noted previously, (−)-1,3-dimethylallene has been assigned the *R* configuration based upon application of Lowe's rule. On similar grounds, Borden and Corey[18] have assigned the *R* configuration to (−)-1,3-di-*tert*-butylallene. Recently, we established that (+)-1,2-cyclononadiene also has the *R* configuration.[12,19] Although in this case Lowe's rule cannot be applied (the wrong configuration would result) because of the conformational dissymmetry of the methylene chain, there is no doubt about the validity of Lowe's rule in the first two cases since the substituents (methyl and *tert*-butyl) have effective cylindrical symmetry. On the other hand, one cannot apply Lowe's rule to 1,3-diethylallene or 1,3-dipropylallene without further considerations, because the ethyl and propyl groups could introduce conformational dissymmetry which might be important in determining the sign of rotation.

Examination of molecular models indicates that the ethyl and propyl groups are sufficiently remote that in most conformations the spatial orientation of one group should not influence the other. As a result, each ethyl (propyl) group must very nearly achieve what might be termed time-averaged conformational symmetry with respect to the pertinent molecular plane of the allene (the CH_2–C–H plane).[20] In this situation, reference to the general sector rule which applies to allenes[13] makes it clear that Lowe's rule is applicable and thus (−)-1,3-diethylallene and (−)-1,3-dipropylallene have the *R* configuration. This assignment was confirmed by comparing the ORD and CD spectra of the four acyclic (−)-allenes (Figure 1); *it is evident that they all must have the same configuration, viz., R.* The contrasting behavior in the case of 1,2-cyclononadiene, where the conformational dissymmetry is of paramount importance,[12] is evident in the ORD–CD curves shown for the *R*-(+) enantiomer (Figure 2).

Regiospecificity. While we were primarily interested in the optical activity of recovered allene, it seemed wise to determine whether or not $Pn_4B_2H_2$ was typical in terms of regiospecificity. Hydroboration of an allene can lead to either a vinyl or an allylic organoborane. In an oxidative work-up, the former yields a ketone and the latter a mixture of allylic alcohol and alkene (by hydrolysis of the labile allylic borane) as is illustrated for 1,2-cyclononadiene in Scheme I. With allene itself, diborane leads to terminal addition (allylic borane).[22] However, several 1,3-dialkylallenes have been found to undergo predominant addition of boron to the central allenic carbon atom with both diborane

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(18) W. T. Borden and E. J. Corey, *Tetrahedron Lett.*, 313 (1969).

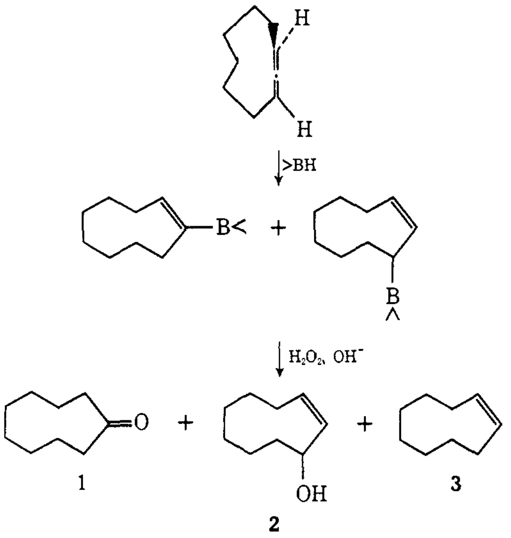
(19) For an alternate method see R. D. Bach, U. Mazur, R. N. Brummel, and L. H. Lin, *J. Amer. Chem. Soc.*, **93**, 7120 (1971).

(20) Similar reasoning indicates that, in general, the configuration of a 1,3-dialkylallene will be correctly predicted by Lowe's rule. Hence the assignment of the *R* configuration to (−)-laballenic acid,[21] $CH_3(CH_2)_{10}CH{=}C{=}CH(CH_2)_3CO_2H$, on the basis of an asymmetric synthesis with a very small optical yield (6.4%) appears to be correct. We should note, however, that the example of 1,2-cyclononadiene must always introduce a note of caution and moreover, it suggests that if one can conformationally restrict an acyclic 1,3-dialkylallene, it may be possible to "violate" Lowe's rule. To this end we examined the rotation of 1,3-dipropylallene in both alkane and perfluoroalkane solvents with the thought in mind that in the latter "alien" (poor) solvent the allene might be somewhat restricted conformationally with the propyl groups approximating the 1,2-cyclononadiene structure. However no significant difference in rotations was found.

(21) S. R. Landor and N. Punja, *Tetrahedron Lett.*, 4905 (1966).

(22) (a) K. A. Saegebarth, U. S. Pat. 3,014,075, *Chem. Abstr.*, **56**, 13095 (1962); (b) H. H. Lindner and T. Onak, *J. Amer. Chem. Soc.*, **88**, 1886 (1966).

Scheme I



and tetrasiamyldiborane.[23] We have found that $Pn_4B_2H_2$ adds to 1,2-cyclononadiene in the same sense but with slightly less selectivity than is shown by tetrasiamyldiborane. These results are summarized in Table III.

Table III. Oxidation of the Organoboranes from the Hydroboration of 1,2-Cyclononadiene

Reagent[a]	Products Relative amounts 1	2	3	Boron addition (central)/ (terminal)	Yield, %	Ref
BH_3[b]	83[c]		17	83/17	77	*d*
$Sia_4B_2H_2$	83	12	5	83/17	78	*e*
$Sia_4B_2H_2$	80	14	6	80/20	92	*f*
$Pn_4B_2H_2$	72	18	10	72/28	85	*f*

[a] Diglyme solvent except as noted. [b] Tetrahydrofuran solvent. [c] Includes 4% cyclononanol from reduction of **1**. [d] Reference 23a,b. [e] Reference 23c. [f] This work.

Discussion

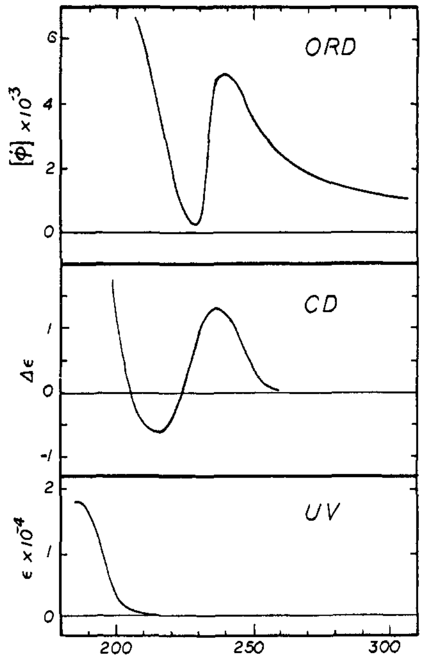
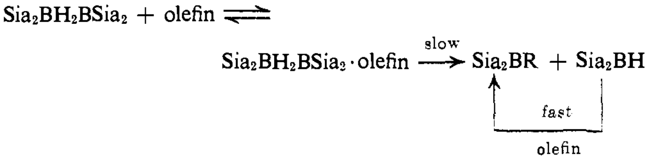


Figure 2. ORD, CD, and uv spectra of 1,2-cyclononadiene.

The use of Brown's reagent for preparation of optically active allenes, introduced by Caserio and her coworkers, is clearly an extremely useful method. The drawbacks are that only moderate activities result and that of course one irrevocably parts with a substantial amount of allene.[24] The advantages are that the method is simple and that many allenes are readily available *via* the cyclopropylidene route from *gem*-dibromocyclopropanes.[26] Moreover, we believe that the preceding results clearly show that 1,3-dialkylallenes will always lead to the same stereochemical outcome: (−)-α-pinene will leave an excess of the *R* allene, even with pinene-deficient reagents. This fact makes it evident that the reaction is not mechanistically vacillant. As a consequence, we were encouraged to examine the mechanistic implications of these hydroborations in light of what is known about hydroboration of olefins in general. In the latter context we found it necessary to reconsider models for hydroboration of olefins before applying any to allenes.

Models for Olefins. Brown[6] has established that solutions of $Pn_4B_2H_2$ are not dissociated to Pn_2BH. Thus it seems certain that hydroboration with $Pn_4B_2H_2$ is kinetically identical to hydroboration with $Sia_4B_2H_2$. For the latter, the rate of reaction is first order in $Sia_4B_2H_2$ and first order in olefins leading Brown to propose that the reaction followed the mechanism shown in Scheme II.[27] Of course the formation of a complex by a pretransition state equilibrium is kinetically unnecessary and no evidence for it has appeared.

Scheme II

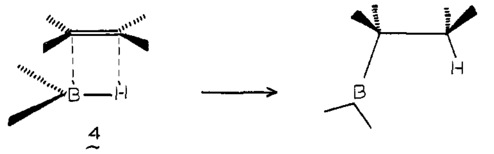


$$Sia_2BH_2BSia_2 + \text{olefin} \rightleftharpoons$$

$$Sia_2BH_2BSia_2\cdot\text{olefin} \xrightarrow{\text{slow}} Sia_2BR + Sia_2BH$$

$$Sia_2BH \xrightarrow[\text{olefin}]{\text{fast}} Sia_2BR$$

Brown suggested that the stereochemical implications of hydroboration would be the same for Pn_2BH and $Pn_4B_2H_2$, hence he selected the former to give a simpler model. He proposed that hydroboration of olefins occurs *via* a four-center transition state **4**, which can be



4

analyzed in terms of the most probable conformation

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(23) (a) D. Devaprabhakara and P. D. Gardner, *J. Amer. Chem. Soc.*, **85**, 1458 (1963); (b) D. S. Sethi and D. Devaprabhakara, *Can. J. Chem.*, **46**, 1165 (1968); (c) D. E. Sethi, G. C. Joshi, and D. Devaprabhakara,*i bid.*, **46**, 2632 (1968).

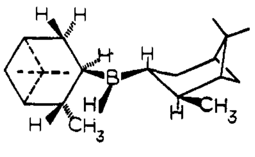
(24) There is the interesting possibility that one might be able to recover the allene (and α-pinene) by cracking recovered alkylboranes in the presence of an inexpensive olefin.[25]

(25) H. C. Brown, "Hydroboration," W. A. Benjamin, New York, N. Y., 1962, pp 150–160.

(26) (a) W. R. Moore and H. R. Ward, *J. Org. Chem.*, **25**, 2073 (1960); (b) L. Skattebøl, *Tetrahedron Lett.*, 167 (1961); (c) W. R. Moore and H. R. Ward, *J. Org. Chem.*, **27**, 4179 (1962); (d) L. Skattebøl, *Acta Chem. Scand.*, **17**, 1683 (1963); (e) L. Skattebøl, *Org. Syn.*, **49**, 35 (1969), and references therein.

(27) H. C. Brown and A. W. Moerikofer, *J. Amer. Chem. Soc.*, **83**, 3417 (1961).

of Pn_2BH.[2b,28] For the reagent derived from (+)-α-pinene, this conformation was taken to be **5** and was



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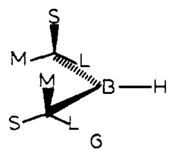

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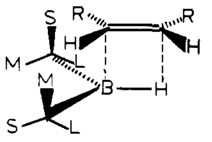

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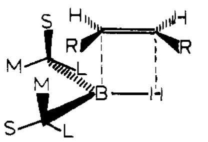
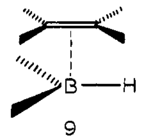


8

represented schematically as **6**. (To be consistent with Brown's proposal, henceforth, we will always refer to reagents derived from (+)-α-pinene—which in the present case would leave *S* allenes.)

This model predicts the correct (predominant) stereochemistry for the products produced from unhindered cis olefins; the proposed transition state **7** clearly would be preferred to **8**. However, the same model applied to trans olefins consistently predicts the wrong stereochemistry. Although Brown suggested that such consistency was empirically useful, he pointed out that the discrepancy presumably stemmed from the fact that olefins, which are less reactive, do not react with $Pn_4B_2H_2$ but actually react with $Pn_3B_2H_3$ by a different mechanism.[15]

Subsequently, two variations on Brown's model have been proposed. Streitwieser[29a] has suggested that the product-forming transition state resembles a π complex, **9**; *i.e.*, Brown's model was shifted from a rectangle to a parallelogram. Varma and Caspi[30] have proposed the use of conformation **10**, which has the "left-hand" pinanyl group rotated *ca.* 90° from Brown's model (the B–H bond of **10** lies on a C_2 axis).



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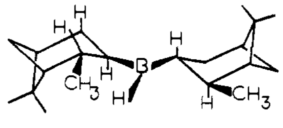
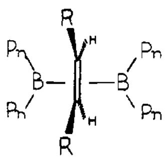


10

Because the Brown model, with or without the proposed variations in it, does not indicate why trans olefins should fail to react, McKenna proposed a model based on $Pn_4B_2H_2$ rather than Pn_2BH.[31] He suggested that the olefin inserts itself edgewise into the center of the tetraalkyldiborane as shown in **11**.

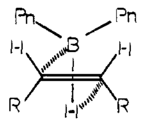


11

Without doubt, trans olefins would find this process impossible because the steric repulsions with the bulky pinanyl groups would be prohibitive for any conformation. Hence trans olefins would be forced to find another reaction pathway. However, so should terminal alkenes ($R_2C{=}CH_2$), which in fact do react with $Pn_4B_2H_2$.[32] A second argument against the detailed geometry suggested by McKenna can be based on the fact that trans olefins *do react* with the hindered $Sia_4B_2H_2$. The reaction is slower than with cis isomers but by only a factor of *ca.* 6 to 10. McKenna's model would require a much greater difference since reaction with trans olefins still would be precluded.

The intervention of the reaction with $Pn_3B_2H_3$ makes it unclear just how unreactive the trans olefins are. The difference in reactivity between cis and trans isomers may not be much greater than with $Sia_4B_2H_2$. Brown[27] suggested that cis olefins are generally more reactive than the trans isomers because of strain in the former. But the greater reactivity of cis olefins is not unique to hydroboration. In other reactions, this difference in reactivity has been explained in terms of transition states in which bulky substitutents in the reagent adding to a cis olefin are not proximate to the substituents on the double bond, giving steric relief not available to the trans isomers.

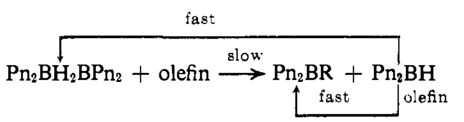
In the case of hydroboration, such steric relief could be gained by the cis olefins if the four-center transition state were skewed as in **12** rather than planar.



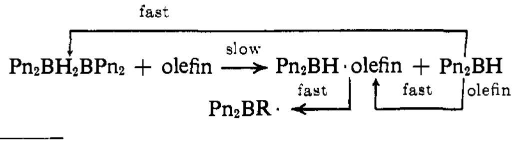
12

Skewing in this fashion would clearly result in the cis olefins being much more reactive than the trans isomers. While **12** is an extreme case, some skewing should be possible (*vide infra*).

Possible Mechanisms. Although we reject McKenna's model, the kinetic data do require that the rate-determining transition state consists of $Pn_4B_2H_2$ and the olefin. But is the rate-determining step also the product-forming step? Focusing attention on this question, we suggest that the two most likely mechanisms are A and B. In A, the product Pn_2BR,



$$Pn_2BH_2BPn_2 + \text{olefin} \xrightarrow{\text{slow}} Pn_2BR + Pn_2BH \qquad \text{(A)}$$



$$Pn_2BH_2BPn_2 + \text{olefin} \xrightarrow{\text{slow}} Pn_2BH\cdot\text{olefin} + Pn_2BH \qquad \text{(B)}$$

$$Pn_2BR\cdot \xleftarrow{\text{fast}}$$

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(28) G. Zweifel, N. R. Ayyangar, and H. C. Brown, *J. Amer. Chem. Soc.*, **84**, 4342 (1962).

(29) (a) A. Streitwieser, Jr., L. Verbit, and R. Bittman, *J. Org. Chem.*, **32**, 1530 (1967); (b) P. R. Jones, Abstracts of the 163rd National Meeting of the American Chemical Society, Boston, April 1972, ORGN 87, has given a symmetry-based argument supporting a π-complex intermediate.

(30) K. R. Varma and E. Caspi, *Tetrahedron*, **24**, 6365 (1968).

(31) D. R. Brown, S. F. A. Kettle, J. McKenna, and J. M. McKenna, *Chem. Commun.*, 667 (1967).

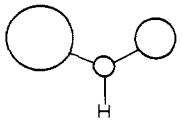
(32) G. Zweifel, N. R. Ayyangar, T. Munekata, and H. C. Brown, *J. Amer. Chem. Soc.*, **86**, 1076 (1964).

is produced *directly* from the rate-determining transition state. In B the rate-determining transition state gives a complex which *subsequently* leads to the product in a fast reaction. In both of these mechanisms, a question arises concerning the fate of the Pn_2BH which is displaced. Does it dimerize or does it react with the olefin? If the monomer is substantially more reactive than the dimer, as is generally assumed, then it seems likely that much, if not all, of the Pn_2BH will be trapped by the olefin when the latter is at relatively high concentrations. If this is so, there will be two stages at which competing olefins can undergo hydroboration. Hence the observed selectivities (relative reactivities) in competition experiments[33] and in kinetic resolutions of chiral substrates will be a composite of these two separate steps. Moreover, to the extent that the Pn_2BH is trapped, mechanism A will have two product-forming transition states which, in principle, could lead to different product ratios.

At this time, we are aware of no evidence which would allow a distinction to be made between mechanisms A and B and we recognize the possibility that both mechanisms may operate. However, Brown-type models have successfully dealt with selectivity in terms of both the relative reactivities of enantiomers and of the stereoselectivity found for product formation from a given substrate. The former *must* refer to the rate-determing step and *may* refer to the product-forming step, while for the latter these conditions are reversed. This fact means that whatever mechanism is followed, the *qualitative implications* of a Brown-type model apply at *both* the rate-determining and product-forming states. Hence it appears to be at least valid to discuss the reaction in terms of the rate-determining step of mechanism A.

It is evident that $Pn_4B_2H_2$ is conformationally more restricted than is Pn_2BH because of the steric interactions between the cis, vicinal-pinanyl groups. Conformations which minimize geminal interactions in the monomer tend to maximize vicinal steric interactions in the dimer. However, contrary to McKenna's[31] supposition, ground-state conformations for Pn_2BH_2-BPn_2 may be poor models for the transition state primarily because the olefin is displacing one of the Pn_2BH groups. As this group leaves, the conformational restrictions in the Pn_2BH group undergoing addition should diminish. For this reason, we will follow Brown's approach and focus attention in the steric requirements of a single Pn_2BH, but we will make two modifications in Brown's model. One concerns the effective shape of the Pn_2BH and the other relates to the orientation of the olefin.

A Simple Model. The models which have been used have been based on some particular conformation of Pn_2BH. Which conformation is "best" is a moot point. In fact no one conformation may be "best" because the *transition-state conformation* should depend somewhat upon the nature of the olefin. Recognizing that what we really want to know is what Pn_2BH looks like at the transition state (*i.e.*, how it interacts with the substrate) we take a somewhat different approach. Both from examination of molecular models and equally from *phenomenological* considerations, it appears to us that all that really can be said about Pn_2BH is that it acts as though it has a less-hindered side on which one pinanyl group is effectively larger than the other. Hence we propose that **13** is an adequate model for Pn_2BH derived from (+)-α-pinene. The circles symbolize the relative steric effects of Pn_2BH when it is viewed from the less-hindered side; *i.e.*, **13** should be used as a one-sided model in which the left-hand portion has the dominant effect (or consider the B–H bond to lie on a C_2 axis). The shape implied by this model is shown in the *conceptional* contour map **14**.



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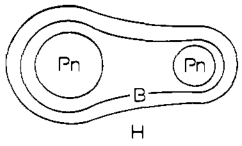

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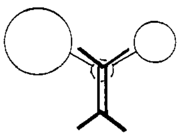
This simple model will correlate the stereochemical results observed for olefins provided that the restriction of a *planar* four-center transition state is removed. Rather than restrict the orientation to **15**, transition state geometries **16** and **17** will also be used. (The olefin could be partially shifted in the sense implied by the π-complex model,[29] without affecting the predictions.) By allowing some skewing, steric interactions generally can be decreased. If relatively little transfer of hydrogen from boron to carbon has occurred at the transition state, there should be a fairly large latitude in the extent of skewing possible. Whether or not skewing is *inherent* in hydroboration is a debatable point. Passage through a skewed transition state might be regarded as antarafacial addition to the BH bond and suprafacial addition to the C=C.



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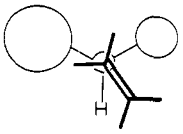

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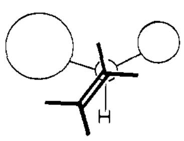

17

Table IV summarizes the application of this model to a variety of olefins. In general, trans olefins are unreactive, but *trans*-cyclooctene, because of its exceptional strain, is able to react with $Pn_4B_2H_2$. Although the cyclooctanol produced is not chiral, the prediction shown in Table IV is verified since (*S*)-(+)-*trans*-cyclooctene, which corresponds to the example in Table IV with the methylene chain away from the reagent, is reduced more readily than the *R*-(−)-enantiomer.[34] Using **13** as a model and allowing for some skewing removes the previous anomaly which arose in explaining[29,30,32] the reversal in the orientations of the olefin for 1-deuterio-1-butene (bulkier group to the right) and 2-methyl-1-butene (bulkier group to the left). In the latter case, one can balance the interaction by skewing a bit.

Allenes. Except for 1,3-di-*tert*-butylallene, the 1,3-dialkylallenes we have examined all react rapidly with $Pn_4B_2H_2$. Thus application of the olefin model should be valid. For the predominant mode of addition,

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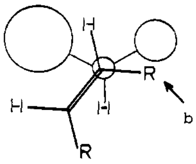
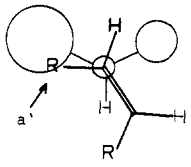
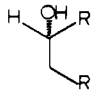
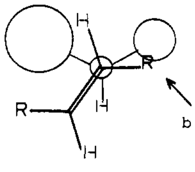
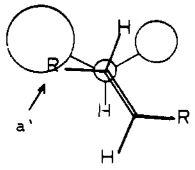
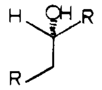
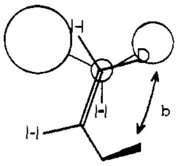
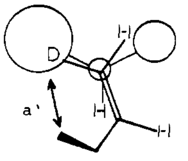
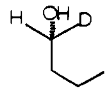
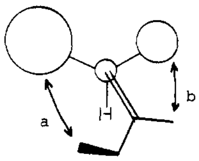
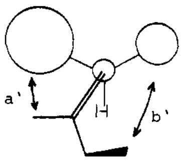
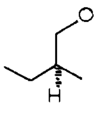
[33] H. C. Brown and A. W. Moerikofer, *J. Amer. Chem. Soc.*, 85, 2063 (1963).

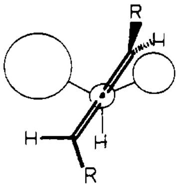
[34] (*R*)-(−)-*trans*-Cyclooctene of 21% optical purity has been obtained by partial hydroboration of the racemic olefin; W. L. Waters, *J. Org. Chem.*, 36, 1569 (1971).

Table IV. Model **13** Applied to Several Simple Olefins

Transition state models: Most favorable[a]	Transition state models: Less favorable[a]	Predominant product	(ref)
 (b < a')			(2, 3)
 (b < a')			(34)[b]
 (b < a')			(29a)
 (a + b < a' + b')			(32)

[a] *Dominant* steric interactions indicated by lettered arrows. [b] (*R*)-(−)-*trans*-Cyclooctene recovered (see text).

attachment of the boron to the central allenic carbon atom, the preferred mode of addition should be as shown in **18**; the *R* enantiomer should be the more reactive, leaving the *S* allene in excess, a prediction which is borne out by the results. Models indicate that the selectivity could be rather high; experimentally, the selectivity is only moderate. We believe that this fact is a consequence of the competing hydroboration in the other regiospecific sense, *viz.*, addition of the boron to a terminal allenic carbon atom. As shown by **19**, the predicted enantiomeric selectivity is reversed; the *S* allene should be the more reactive (with the lower *R* group away from the reagent). The net enantiomeric selectivity is thus determined by the regiospecificity; *R* allene is selectively removed because the predominant mode of addition involves attachment of the boron to the central allenic carbon atom.



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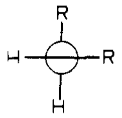

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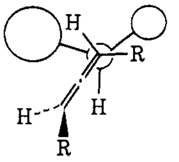

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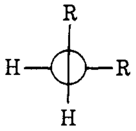

S

Another point of great interest (and practical value) concerns the variation in enantiomeric selectivity from allene to allene. Unfortunately, the optical purities of the allenes are not known; however we can make some reasonable estimates. Consideration of the results of the dimerization of optically active 1,2-cyclononadiene has led to an estimate[35] of $[\phi]_D$ *ca.* 176° for the molecular rotation of the optically pure allene. Brewster's model of optical activity[11] leads to an estimated molecular rotation[36] of $[\phi]_D$ *ca.* 112° for 1,3-dimethylallene. Assuming that the other optically pure acyclic allenes have molecular rotations which are not greatly different from that of 1,3-dimethylallene,[37] the optical purities obtained

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(35) (a) W. R. Moore, R. D. Bach, and T. M. Ozretich, *J. Amer. Chem. Soc.*, **91**, 5918 (1969). (b) The estimated specific rotation of optically pure 1,2-cyclononadiene is $[\alpha]^{25}_D$ ~175° (CH_2Cl_2) corresponding to $[\alpha]^{25}_D$ ~144° (pentane).

(36) This estimate is for pentane solutions, it may be somewhat low (see ref 37).

(37) 1,3-Diethylallene and 1,3-dipropylallene should have nearly identical molecular rotations which should be close to that for laballenic acid,[38] which has a molecular rotation of $[\phi]_D$ 132°. Brewster's method assigns a lower polarizability to *tert*-butyl than to methyl and this leads to a predicted value of $[\phi]_D$ *ca.* 90° for 1,3-di-*tert*-butylallene. This value is *less* than the highest value we observed for this allene, *viz.* $[\phi]_{578}$ 123° (pentane), employing the asymmetric synthesis of Borden and Corey.[18]

(38) M. O. Bagby, C. R. Smith, Jr., and I. A. Wolff, *Chem. Ind.* (*London*), 1861 (1964); *J. Org. Chem.*, **30**, 4227 (1965).

apparently increase in the order 1,3-dimethylallene < 1,2-cyclononadiene < 1,3-di-*tert*-butylallene < 1,3-diethylallene < 1,3-dipropylallene. Since 1,3-di-*tert*-butylallene appears to have been reduced largely by the less selective $Pn_3B_2H_3$, its optical purity must be substantially less than it would be if $Pn_4B_2H_2$ were the active agent.

The methylene chain of 1,2-cyclononadiene is tied back, effectively blocking reaction at one face of each double bond, but leaving the other face nearly as open as in 1,3-dimethylallene, for which steric effects are at a minimum. Both 1,3-diethyl- and 1,3-dipropylallene can fit on the face of the reagent as indicated in the model **18**, but in so doing, some of the conformational freedom of the side chain on the double bond being reduced must be lost; accordingly, as would be expected, both compounds react more slowly than 1,3-dimethylallene. Moreover it is apparent that the loss of conformational freedom will be greater for the *S* allene than for the *R* allene because the "preferred" *R* transition state minimizes the steric interactions.

The substantially higher optical purities obtained for 1,3-diethyl- and 1,3-dipropylallene indicate that either would be preferable to 1,3-dimethylallene in stereochemical studies. Additionally, it seems likely that one might obtain still higher optical purities with other allenes; *e.g.*, 1,3-diisopropylallene should lead to an enhancement of the conformational effect discussed above and yet (hopefully) still would not be too hindered to react with $Pn_4B_2H_2$.

Pinene Deficient Reagents. Hydroboration with $Pn_3B_2H_3$ proceeds in the same predominant stereochemical sense as with $Pn_4B_2H_2$. It seems probable that reaction involves a terminal B–H bond of the diborane rather than a bridging B–H bond. In any event, the allene must "see" a reagent having the same general shape as that employed for the Pn_2BH model although the $Pn_3B_2H_3$ model presumably is less sharply defined because the selectivity diminishes. Again it is likely that the selectivity is diminished by competing regiospecific modes of hydroboration.

The stereochemical differences which arise with the $Pn_2B_2H_4$ reagents must be still more subtle and we will not attempt to analyze these relatively unselective reagents. However the fact that the $Pn_2B_2H_4$ reagents functioned in the same stereochemical way as the more selective $Pn_4B_2H_2$ is worth noting and may prove to be of importance in dealing with very hindered cases.

Experimental Section[39]

Preparation of Allenes. Racemic 1,3-dimethylallene, 1,3-diethylallene, 1,3-di-*n*-propylallene, and 1,2-cyclononadiene were prepared by treatment of the appropriate *gem*-dibromocyclopropane with methyllithium in ether.[26] In the case of 1,3-dimethylallene, material free of ether (which is difficult to remove by distillation) can be obtained by using diglyme as a solvent.

Following the methods of Borden and Corey,[18] racemic 1,3-di-*tert*-butylallene was prepared by reduction of 1,3-di-*tert*-butylpropargyl alcohol with $LiAlH_4$–$AlCl_3$. Resolution of the alcohol,[40] conversion to the tosylate, reduction of the latter with $LiAl(OCH_3)_2H_2$ and glc separation gave the optically active allene, $[\alpha]^{25}_{578}$ −80° (*c* 0.2, pentane). This material was used for the ORD–CD spectra.

Reaction of Allenes with Tetra-3-pinanyldiborane. The following reaction is typical. Boron trifluoride etherate (0.316 g, 2.22 mmol) in 2 ml of diglyme (distilled from $LiAlH_4$) was added slowly *via* syringe to a stirred slurry of (−)-α-pinene (0.604 g, 4.44 mmol) and sodium borohydride (0.070 g, 1.85 mmol) in 2 ml of diglyme at 0°. Within 1 hr, a thick white precipitate formed. After 4 hr at 0°, a precooled solution (0°) of 1,3-diethylallene (0.320 g, 3.33 mmol) and *n*-octane (internal standard, 0.0190 g, 0.167 mmol) in 1 ml of ether was added as fast as possible *via* syringe to the stirred $Pn_4B_2H_2$ reagent. As the reaction proceeded, aliquots were removed from the reaction mixture, quenched with water, extracted with pentane, and set aside for subsequent analysis. Glc analysis indicated that the reaction was complete within 20 min. The reaction mixture was quenched with water and pentane was added. The pentane layer was separated, washed with water, dried (K_2CO_3) and concentrated. Bulb-to-bulb distillation at room temperature (1 mm) followed by preparative glc gave optically active 1,3-diethylallene, $[\alpha]^{22}_{578}$ −54.9° (*c* 0.310, pentane).

The results of this run as well as those obtained from the reactions of the other allenes are summarized in Table I.

The glc conditions employed for handling the allenes throughout this study are given in the order allene, analytical column (preparative column): 1,3-dimethylallene, D, 25° (A, 25°); 1,3-diethylallene, E, 25, and F, 45° (B, 45°); 1,3-di-*n*-propylallene, F, 75° (C, 75°); 1,3-di-*tert*-butylallene, F, 75°, and G, 85° (C, 75°); 1,2-cyclononadiene, G, 75° (B, 90°). The glc columns were as follows: A (183 × 0.4 cm, 20% Silicone 710); B (92 × 0.4 cm, 10% Silicone 710—5% KOH); C (92 × 0.4 cm, 20% Apiezon M); D (366 × 0.2 cm, 5% tetraethylene glycol—5% Carbowax 600—5% KOH); E (183 × 0.2 cm, 1% SE-30); F (102 × 0.2 cm, 10% Apiezon M); G (183 × 0.2 cm, 5% Carbowax 20M). All used 80–100 mesh Chromosorb P (A, B, D, E, F, G) or Chromosorb (C) in glass (A, B) or aluminum tubing (C, D, E, F, G).

Reaction of Allenes with Tri-3-pinanyldiborane. The following general procedure was employed. Boron trifluoride etherate (0.316 g, 2.22 mmol) in 2 ml of diglyme (distilled from $LiAlH_4$) was added slowly *via* syringe to a stirred slurry of (−)-α-pinene (0.457 g, 3.33 mmol) and sodium borohydride (0.070 g, 1.85 mmol) in 2 ml of diglyme at 0°. Within 1 hr, a white precipitate formed After 4 hr at 0°, a precooled solution (0°) of 1,3-diethylallene (0.160 g, 1.67 mmol) and *n*-octane (internal standard, 0.0180 g, 0.158 mmol) in 1 ml of ether was added as fast as possible *via* syringe. After 5.5 min the reaction mixture was quenched with water, analyzed by glc and worked-up as above. Preparative glc gave optically active 1,3-diethylallene, $[\alpha]^{22}_{578}$ −28.5° (*c* 0.68, pentane).

To prepare the aged reagent, $Pn_3B_2H_3$ was prepared as described above. One hour after the boron trifluoride etherate was added, the slurry was allowed to warm to room temperature and then was stirred for 14 hr under nitrogen. The slurry was then cooled to 0° and the reaction with 1,3-diethylallene was carried out as above. All of the results obtained with $Pn_3B_2H_3$ are summarized in Table II.

Reaction of Allenes with Di-3-pinanyldiborane. A typical experiment follows. Boron trifluoride etherate (0.316 g, 2.22 mmol) in 2 ml of dry diglyme (distilled from $LiAlH_4$) was added slowly *via* syringe to a stirred slurry of (−)-α-pinene (0.302 g, 2.22 mmol) and sodium borohydride (0.071 g, 1.86 mmol) in 2 ml of diglyme at 0°. No white precipitate was formed with this reagent. After 4 hr at 0°, a precooled solution (0°) of 1,3-diethylallene (0.320 g, 3.33 mmol) and *n*-octane (internal standard, 0.011 g, 0.096 mmol) in 1 ml of ether was added dropwise *via* syringe. After 4.8 min the reaction mixture was quenched with water, analyzed and worked-up as above. Preparative glc gave optically active 1,3-diethylallene, $[\alpha]^{22}_{578}$ −10.2° (*c* 1.03, pentane).

To prepare the aged reagent, $Pn_2B_2H_4$ was prepared as described above. One hour after the addition of the boron trifluoride etherate, the solution was allowed to warm to room temperature and was stirred for 14 hr under nitrogen. The solution was then cooled to 0°, 1,3-diethylallene was added and the reaction was continued as above. The results of all experiments with $Pn_2B_2H_4$ are given in Table II.

Hydroboration–Oxidation of 1,2-Cyclononadiene. Hydroborations with tetrasiamyldiborane were carried out at 0° in diglyme in the usual way.[23c] The following quantities of reagents were used: 32 mg (0.8 mmol) of sodium borohydride, 154 mg (2.2 mmol) of 2-methyl-2-butene, 158 mg (1.1 mmol) of boron trifluoride etherate, and 122 mg (1.00 mmol) of 1,2-cyclononadiene. Hydroborations with tetra-3-pinanyldiborane were carried out as described above.

The following oxidative procedure was employed for all hydro-

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[39] Optical rotations were routinely measured with a Zeiss photoelectric precision polarimeter. ORD and CD measurements were made with a Cary Model 60 spectropolarimeter and ultraviolet measurements were made with a Cary Model 14 spectrophotometer. Reactions were carried out under nitrogen whenever air-sensitive materials were involved.

[40] We wish to thank Professor F. D. Greene for a generous supply of the racemic alcohol.

borations. When the hydroboration was complete, the reaction flask was fitted with a short reflux condenser and several drops of 1 *N* NaOH solution was added. Then 2 drops of 30% H_2O_2 was added causing the reaction mixture to reflux. The pH of the mixture was maintained at *ca.* 9 by dropwise addition of 1 *N* NaOH as 3 ml of 30% H_2O_2 was added at a rate which maintained reflux. Stirring was continued for 15 min after all of the H_2O_2 had been added. Sodium chloride (1 g) was added and the products were extracted with three 2-ml portions of ether. The ether solution was washed with saturated sodium chloride solution, dried ($MgSO_4$), and analyzed by glc (183 × 0.2 cm, 5% Carbowax 20M, 50 to 180°, *n*-nonane internal standard). The yields of the products, identified by comparison with authentic materials, are reported in Table III.

Fenton's Reagent. II. Reactions of Carbonyl Compounds and α,β-Unsaturated Acids[1]

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Abstract: Carbonyl compounds such as acetone are readily attacked by hydroxyl radicals generated by the reaction of Fe^{2+} and H_2O_2, but the resulting carbonyl conjugated radicals are reduced to starting material by additional Fe^{2+}. As hydroxyl radical traps, they thus retard the oxidation of methanol, and rate constants for hydroxyl radical reactions derived from the competitive inhibition are in good agreement with those from radiation chemistry. Hydroxyl radicals add readily to the double bonds of α,β-unsaturated acids, and the resulting radicals are also reduced with a net addition of water; *e.g.*, maleic acid is converted to malic acid. The acids inhibit alcohol oxidation by trapping both hydroxy and α-hydroxyalkyl radicals, the latter process providing an interesting possible synthesis of lactones.

In their investigation of Fenton's reagent (ferrous ion–hydrogen peroxide) reported in 1949,[3] Merz and Waters noted that substrates such as acetone were not oxidized and had no effect on the stoichiometry of the Fe^{2+}–H_2O_2 reaction but markedly retarded the oxidation of such other materials as methanol. They proposed that in these cases hydroxyl radical attack on the substrate indeed takes place, but that the resulting radicals are reduced back to starting material by ferrous ion.

This paper describes a reexamination of such systems, using the analysis which we have shown to be successful for interpreting the behavior of aliphatic alcohols[4] and also a study of the related reaction of Fenton's reagent with α,β-unsaturated acids.

Kinetic Scheme. If H_2O_2 is added to an aqueous system containing an organic substrate and excess Fe^{2+} at pH 0–2, the hydroxyl radicals generated attack the substrate, and the subsequent course of the reaction and stoichiometry (moles of Fe^{2+} oxidized/mole of H_2O_2 added: $\Delta[Fe^{2+}]/\Delta[H_2O_2]$) depend upon the fate of the organic radicals so produced. For a system containing a variety of C–H bonds, the postulated reaction steps are the following.[5]

$$Fe^{2+} + H_2O_2 \xrightarrow{k_1} Fe^{3+} + HO^- + HO\cdot \qquad (1)$$

$$HO\cdot + Fe^{2+} \xrightarrow{k_2} Fe^{3+} + HO^- \qquad (2)$$

$$HO\cdot + R_iH \xrightarrow{k_{3i}} H_2O + R_i\cdot \qquad (3a)$$

$$HO\cdot + R_jH \xrightarrow{k_{3j}} H_2O + R_j\cdot \qquad (3b)$$

$$HO\cdot + R_kH \xrightarrow{k_{3k}} H_2O + R_k\cdot \qquad (3c)$$

$$R_i\cdot + Fe^{3+} \xrightarrow{k_4} Fe^{2+} + \text{product} \qquad (4)$$

$$2R_j\cdot \xrightarrow{k_5} \text{product (dimer)} \qquad (5)$$

$$R_k\cdot + Fe^{2+} \xrightarrow{k_6} Fe^{3+} + R_k^- \xrightarrow{H^+} R_kH \qquad (6)$$

It is assumed the radicals produced in (3) behave as belonging to three distinct classes: those oxidized by Fe^{3+}, $R_i\cdot$; those which are inert and dimerize, $R_j\cdot$; and those which undergo reduction by Fe^{2+}, $R_k\cdot$. As proposed by Merz and Waters and demonstrated further in our previous work, the α-hydroxy radicals from alcohols belong to the first group, and simple carbon radicals (such as those arising from hydroxyl radical attack on remote C–H bonds of alcohols) belong to the second. However, addition of cupric ion makes the latter oxidizable as well

$$R\cdot + Cu^{2+} \longrightarrow \text{products} + Cu^+ \xrightarrow{Fe^{3+}} Cu^{2+} + Fe^{2+} \qquad (7)$$

Thus the effect of added cupric ion on the Fenton's reagent system provides a useful tool for its analysis. If we assume with Merz and Waters that radicals from acetone and similar substrates belong to the third, reducible group, and consider a system containing methanol (R_iH) and acetone (R_kH), application of usual steady-state kinetics to eq 1–6 yields the stoichiometric equation

$$\frac{\Delta[Fe^{2+}]}{2\Delta[H_2O_2] - \Delta[Fe^{2+}]} = \frac{k_2[Fe^{2+}]}{k_{3i}[R_iH]} + \frac{k_{3k}[R_kH]}{k_{3i}[R_iH]} \qquad (8)$$

If ferrous ion consumption is measured in a series of

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[1] Taken from the Ph.D. Thesis of G. El-Taliawi, Columbia University, 1972. Support of this work by a grant from the National Science Foundation is gratefully acknowledged.

[2] Address correspondence to this author at the University of Utah.

[3] J. H. Merz and W. A. Waters, *J. Chem. Soc.*, 515 (1949).

[4] C. Walling and S. Kato, *J. Amer. Chem. Soc.*, **93**, 4275 (1971).

[5] k_{3i}, k_{3j}, and k_{3k} replace k_{31}, k_{32}, and k_{33} in our previous treatment.[4]