

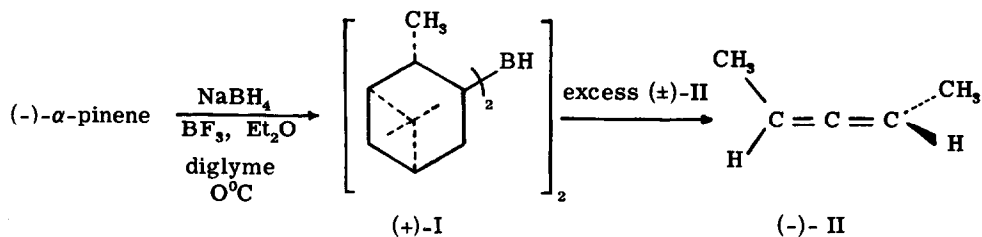
RESOLUTION AND ABSOLUTE CONFIGURATION OF 1,3-DIMETHYLLALLENE

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We wish to report a simple one-step method for the partial resolution of racemic allenes based on the procedure of asymmetric hydroboration developed by H. C. Brown and coworkers⁽¹⁾. Hydroboration of (-)- α -pinene in diglyme leads to (+)-sym-tetraiso-pinocampheyldiborane^(1b), I, which has been shown to be a highly stereoselective hydroborating agent and can be used to prepare certain optically active alcohols and alkenes in high optical purity^(1c). Utilizing this reagent for the hydroboration of excess 1,3-dimethylallene, II, we anticipated that the recoverable allene would be enriched in one enantiomer. This was confirmed by experiment. In a typical run, a suspension of (+)-I in



diglyme was prepared from (-)- α -pinene [α]_D²⁴ = -55.5° (CHCl_3), and diborane (formed in situ from sodium borohydride and boron trifluoride etherate); a two-fold excess of racemic II was then added to the reaction mixture maintained at 0° . After 2-3 hours, the unreacted allene was recovered by flash distillation at reduced pressure followed by fractional

distillation giving material of specific rotation $[\alpha]_D \sim -17^\circ$ (ether). The level of asymmetric induction varied with the particular reaction conditions, as summarized in Table 1, and the lowest levels of activity were obtained on hydroboration of II with a borane mixture prepared from (-)- α -pinene and BH_3 in tetrahydrofuran⁽²⁾. The single advantage of this method of partial resolution is its simplicity. In one step, a level of asymmetric induction is achieved that compares favorably with that obtained in the synthesis recently developed by Jones and coworkers⁽³⁾.

TABLE 1
Specific Rotations in the Partial Resolution of
1, 3-Disubstituted Allenes by Asymmetric Hydroboration

α -Pinene (moles)	BH_3 (moles)	RCH=C=CHR (moles)	$[\alpha]_D^a$	Time (hr) ^b
0.225 ^c	0.113 ^d	0.225 ^e	-21.0 ^o	3
0.149 ^c	0.075 ^d	0.147 ^e	-18.7 ^o	3
0.100 ^c	0.050 ^d	0.100 ^e	-43.8 ^o	4
0.086 ^f	0.043 ^d	0.086 ^e	+4.4 ^o	1.5
0.149 ^c	0.075 ^d	0.149 ^e	-17.7 ^o	3
0.026 ^{c, g}	0.013 ^d	0.026 ^e	-	3
0.163 ^c	0.081 ^h	0.147 ^e	-7.8 ^o	-
0.139 ^c	0.069 ^h	0.139 ^e	-7.6 ^o	2.5
0.012 ^c	0.006 ^h	0.012 ⁱ	-180 ^o	3

a In ether. b Optimum yields (up to 100% of recoverable allene) were achieved in 3 hr. c (-)- α -Pinene, $[\alpha]_D^{24} = -55.3^\circ$ ($c = 8$, CHCl_3). d Based on a 4:3 mole ratio of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ to NaBH_4 in diglyme as solvent. e $\text{CH}_2\text{CH}=\text{C}=\text{CHCH}_3$ containing some diethyl ether. f (+)- α -Pinene, $[\alpha]_D^{23} = +40.8^\circ$ ($c = 3$, CCl_4). g 7.4 mmoles of II were consumed and 4.0 mmoles of (-)- α -pinene were recovered. h In THF. i $\text{C}_6\text{H}_5\text{CH}=\text{C}=\text{CHC}_6\text{H}_5$.

The absolute configuration of II could in principle be deduced from the configuration of the transition state for asymmetric hydroboration if this were known with any certainty. A mechanism of asymmetric induction in hydroborations with active I has been described⁽⁴⁾, and other less-rigorous transition-state models of hydroboration have been proposed by Brown *et al.*,^(1a-d) and by Streitwieser *et al.*⁽⁵⁾. However, none of these models satisfactorily accounts for the course of asymmetric induction observed with trans or hindered alkenes. In such cases, the reaction appears to be mechanistically complex. Displacement of α -pinene is observed in amounts suggestive that I is not directly involved in hydroboration of the alkene but undergoes a slow dissociation to α -pinene and tri-isopinocampheylidiborane, which subsequently reacts with the alkene^(1a). In the hydroboration of II with a suspension of I in diglyme, displacement of α -pinene was indeed observed in amount corresponding to one half the molar equivalent of allene consumed. The reaction is therefore complex and appears to involve more than one type of asymmetric borane. Hence, we abandoned attempts to predict the configuration of (-)-II from transition-state models of hydroboration.

We assume, however, that the stereoselectivity developed in the transition state of hydroboration of II is similar in kind to that developed in the hydroboration of the structurally related compound, 1,3-diphenylallene, III. Under comparable reaction conditions, therefore, the configuration of the enantiomer enriched in recovered II is expected to be the same as that enriched in recovered III. Hydroboration of excess racemic III with a borane mixture prepared from (-)- α -pinene and BH_3 in tetrahydrofuran (see Table 1) led to the recovery of optically active III of rotation $[\alpha]_{\text{D}}^{26} = -180^\circ$ (CHCl_3), the configuration of which is known to be R⁽⁶⁾. We conclude, therefore, that (-)-II obtained by asymmetric

hydroboration under the same conditions also has the R configuration. This assignment of configuration has been established independently by Jones and Walbrick⁽⁷⁾, and was predicted by Brewster⁽⁸⁾ who has calculated the rotation of optically pure R-(-)-II to be $[\alpha]_D = -174^\circ$. From the results of a related study on the stereochemistry of methoxymercuration of (-)-II, we have estimated the optical purity of II of rotation -15.9° to be 7%⁽⁹⁾, in fair agreement with the calculated value of 9%.

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