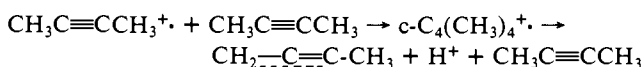


radical observed. The reactions detected are summarized as follows:



Similar ESR studies have been carried out on other substituted acetylenes such as methylacetylene, ethylacetylene, and diethylacetylene and tentative evidence has been obtained for the analogous cycloaddition of methylacetylene radical cation to methylacetylene.

Our INDO calculations¹¹ of $\text{c-C}_4(\text{CH}_3)_4^{\cdot+}$ resulted in a rectangle (D_{2h}) structure at the optimized geometry where the semi-occupied molecular orbital (SOMO) is b_{2g} , similarly to the ab initio calculations of cyclobutadiene.⁶ The experimental proton hf splitting was favorably reproduced by the present calculations (cf. Figure 2). Assuming the sandwich structure I, any reasonable ¹H hf splitting was not obtained by the calculations. These results further support a formation of $\text{c-C}_4(\text{CH}_3)_4^{\cdot+}$. By employing the frontier orbital interaction scheme,¹² the cycloaddition can be represented in terms of the interaction of the SOMO of $\text{DMA}^{\cdot+}$ with the HOMO (highest occupied molecular orbital) of DMA. It should be noted that the concerted [2 + 2] suprafacial process is symmetry forbidden for the $\pi-\pi^*$ DMA cycloaddition (i.e., HOMO-LUMO interaction). The analogous cycloaddition reaction, but initiated by the monomer radical anion, has been observed for tetrafluoroethylene in solid tetramethylsilane matrix by ESR spectroscopy: $\text{C}_2\text{F}_4 + \text{C}_2\text{F}_4^{\cdot-} \rightarrow \text{c-C}_4\text{F}_8^{\cdot-}$.¹³

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Asymmetric Synthesis of the Diastereomeric 1-(2-Cyclohexenyl)-1-alkanols in High Optical Purity via a Stereochemically Stable Allylic Borane, B-2-Cyclohexen-1-yldiisopinocampheylborane

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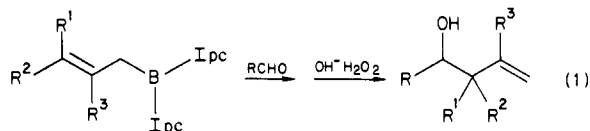
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The hydroboration of 1,3-cyclohexadiene by (+)- and (-)-diisopinocampheylborane at -25°C provides the enantiomeric B-2-cyclohexen-1-yldiisopinocampheylboranes in 94% ee. These enantiomeric allylic boranes, the first such derivatives to be synthesized, retain their stereochemical identity under these conditions in spite of the rapid allylic rearrangement that such compounds normally undergo. They are readily oxidized to the enantiomeric 2-cyclohexen-1-ols in 93% ee, making these derivatives readily available. Finally, the parent boranes react readily with acetaldehyde and other representative aldehydes to provide the corresponding 1-(2-cyclohexenyl)-1-alkanols in 100% erythro selectivities and 94% ee.

Hoffmann and his co-workers have utilized allylboronic esters prepared from optically active glycols to achieve the asymmetric synthesis of homoallylic alcohols.¹ Unfortunately, the preferred

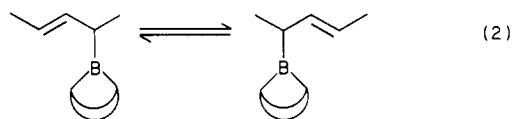
chiral auxiliary must be synthesized by "multistep" procedure. Moreover, the optical purities achieved are usually only in the 60-80% ee range.

We discovered that simple allylic derivatives (Ipc_2BR : R = allyl,² 2-methylallyl,³ 3,3-dimethylallyl;⁴ Ipc = isopinocampheyl) are readily synthesized and yield the homoallylic alcohols with optical purities in the range of 88-96% ee⁵ (eq 1).



There is considerable interest in extending such asymmetric syntheses to the enantioselective synthesis of diastereomers. Indeed, there are several reports describing excellent diastereoselective reactions of allyl metals with aldehydes.⁶ However, most of the literature involves use of optically inactive allyl metals. In only two cases have optically active allyl metals been used.^{7,8}

The B-crotyl derivatives are known to undergo internal allylic isomerization.⁹ The rate of isomerization of these intermediate derivatives varies greatly: allyl- $\text{BR}_2 >$ allyl- $\text{B}(\text{OR}') >$ allyl- $\text{B}(\text{OR}')_2$. Further, the rate of reaction with aldehydes varies in the same order: allyl- BR_2 reacts readily at -78°C ,² the allyl- $\text{B}(\text{OR}')_2$ at -15°C \rightarrow room temperature, and the allyl- $\text{B}(\text{OR}')_2$ at room temperature.⁷ The optical purity achieved is greater the lower the reaction temperature. Thus, the problem in using our approach over the less reactive $\text{RB}(\text{OR}')$ and $\text{RB}(\text{OR}')_2$ was the lack of any knowledge about the practical synthesis of optically active allyldialkylborane ($\text{R}^*\text{BR}'_2$). Such dialkylboranes are known to undergo rapid allylic rearrangement, even at relatively low temperature^{9a} (eq 2).



In a symmetrical system, each allylic shift would produce the enantiomer, resulting in a rapid racemization. Accordingly, the first hurdle in examining the feasibility of extending our allylboration to the synthesis of optically active diastereomers involved testing the possibility of synthesizing an optically active chiral allylborane, R^*BIpc_2 , to see if such compounds could retain their optical activity sufficiently long to be useful for asymmetric synthesis.

1,3-Cyclohexadiene was treated with Ipc_2BH [from (+)- α -pinene] at -25°C . The reaction product was oxidized at 0°C with trimethylamine N-oxide.¹⁰ There was obtained a 92:8 mixture of (S)-(-)-2-cyclohexen-1-ol, $[\alpha]_D^{23} -104.5^\circ$ (c 1.0, CHCl_3), 93% ee,¹¹ and 3-cyclohexen-1-ol (eq 3).

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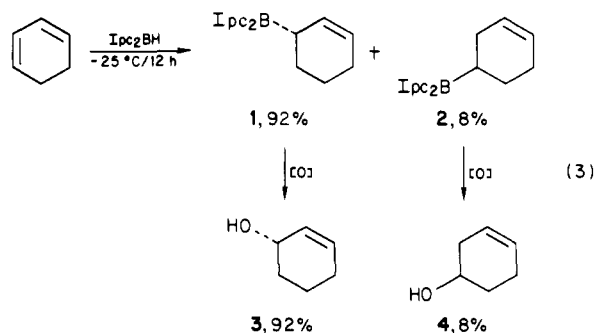
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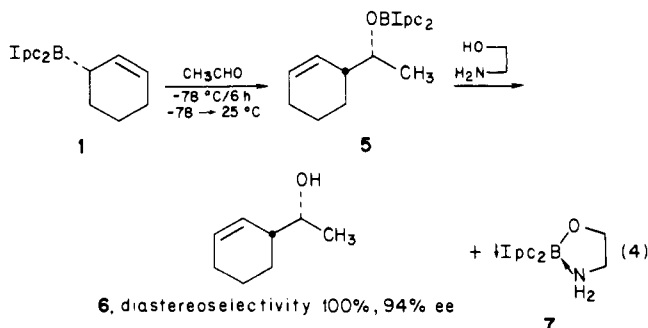
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Consequently, hydroboration occurs predominantly in the allylic position¹² and the optical activity is predominantly retained, even at 0 °C.

Similarly, hydroboration of 1,3-cyclohexadiene by Ipc_2BH [from (-)- α -pinene] gave (*R*)-(+)-2-cyclohexen-1-ol.

The two reagents, *B*-2-cyclohexen-1-yldiisopinocampheylboranes [from (+)- α -pinene and (-)- α -pinene], react readily with acetaldehyde at -78 °C. Only the allylic derivative **1** reacts. The minor homoallylic derivative **2** does not, making the separation of the isomeric impurities extremely simple. The reagent from (+)- α -pinene yields a borinic ester **5**, which reacts with ethanolamine to provide (1*R*,1'*R*)-(+)-1-(2-cyclohexenyl)-1-ethanol in 94% ee and 100% erythro selectivity (eq 4).



The other isomer, (1*S*,1'*S*)-(-)-1-(2-cyclohexenyl)-1-ethanol, is obtained from the reagent derived from (-)- α -pinene.

Catalytic hydrogenation (5% Pt on C) of (+)-1-(2-cyclohexenyl)-1-ethanol to (*R*)-(-)-1-cyclohexyl-1-ethanol, $[\alpha]^{23}_{\text{D}} -4.79^\circ$ (neat), established the absolute configuration of the asymmetric carbon bearing the hydroxyl group.¹³ The absolute configuration of the other chiral center was readily determined by tosylation, followed by reductive detosylation of (+)-1-(2-cyclohexenyl)-1-ethanol to (*R*)-(+)-3-ethylcyclohexene, $[\alpha]^{23}_{\text{D}} +20.73^\circ$ (neat).¹⁴

The following experimental procedure is representative. All operations were carried out under nitrogen.¹⁵ Diisopinocampheylborane (Ipc_2BH) was prepared from (-)- α -pinene following the reported procedure.¹⁶ To the stirred suspension of Ipc_2BH (25 mmol) in THF at -25 °C was added dropwise 2.4 mL (25 mmol) of 1,3-cyclohexadiene. Monohydroboration of the diene was complete after stirring the reaction mixture at -25 °C for 12 h, as indicated by the disappearance of the solid Ipc_2BH and ¹¹B NMR ($\delta +80$) examination of the solution. The orga-

norborane **1** was cooled to -78 °C and treated (dropwise addition) with 1.4 mL (25 mmol) of acetaldehyde. The contents were stirred at -78 °C for 6 h, the dry ice-acetone bath was removed, and the mixture was allowed to warm to room temperature. ¹¹B NMR indicated formation of borinate **5** ($\delta +56$). Excess α -pinene and THF were removed under reduced pressure (25 °C/18 mm/1 h, 0.05 mm/6 h) and the residue was then dissolved in dry *n*-pentane (15 mL). The borinate **5** was cooled to 0 °C and treated with 1.5 mL (25 mmol) of ethanolamine. The contents were stirred at 0 °C for 0.5 h and allowed to warm to room temperature. ¹¹B NMR ($\delta +13$) of the mixture indicated formation of the ethanolamine adduct **7**, a white crystalline solid, which separated after stirring the contents at 25 °C for 1 h. The mixture was cooled to 0 °C and filtered and the solid washed with cold pentane (2 × 10 mL). The residue, following removal of the solvent from the combined filtrate, was distilled to provide 1-(2-cyclohexenyl)-1-ethanol: bp 82 °C (18 mmHg); 2.07 g (66% yield); $[\alpha]^{23}_{\text{D}} -29.17^\circ$ ($l = 0.5$, neat), 94% ee.¹⁷

No difficulty was observed in extending the synthesis to other representative aldehydes, such as propionaldehyde, 2-methylpropionaldehyde, 2,2-dimethylpropionaldehyde, acrolein, and benzaldehyde. In all cases comparable optical purities and erythro diastereoselectivities were realized.

It is evident that this development establishes the feasibility of synthesizing chiral allyldiisopinocampheylboranes, R^*BIpc_2 , and thus makes available a "one-pot" procedure for carbon-carbon bond formation, with 100% diastereoselection and excellent enantiomeric excess. The selectivity is for the erythro isomer, which nicely complements the existing methods for preparing the three isomers.^{7,8} Further, the homoallylic alcohols formed can be ring opened to the corresponding acyclic erythro products, thus greatly expanding the range of applicability of the allylboration reaction.

Acknowledgment. Financial support from the National Institutes of Health is gratefully acknowledged (Grant GM 10937-20). The Varian XL-200 spectrometer was purchased with funds from the National Science Foundation Grant CHE-8004246. This support is also gratefully acknowledged.

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Potential of Mean Force for the Stacking of Phenyl Rings in Aqueous Solution

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Recently, diverse theoretical studies of hydrophobic interactions involving liquid state computer simulation and in some cases potential of mean force determinations¹⁻⁸ have given computational support to the idea⁹ that the hydrophobic effect can act over longer

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