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Preliminary communication

STEREOCHEMISTRY OF THE ALLENE IN THE CONVERSION OF ETHYNYLALKANOL ACETATES INTO ALLENES VIA ORGANOBORANES*

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Summary

Sequential treatment of *R*-(+)-1-octyn-3-ol acetate with n-butyllithium, tri-n-butylborane and acetic acid produces 5,6-dodecadiene which is enriched in the *S*-(+) enantiomer. The migration of the alkyl group from boron thus occurs preferentially *anti* to the leaving group.

Trialkylboranes are well known for the transformation of the alkyl group into a variety of products with complete retention of configuration [1, 2]. These reactions are believed to occur through a rearrangement of an organoborate anion in which one of the groups contains a suitable leaving group (eq. 1—3). While there is a great amount of data on the stereochemistry of the transferring alkyl group, very little is known about the stereochemistry of the carbon containing the leaving group. The rearrangement could occur simultaneously with the X group leaving, giving inversion (S_N2 type) (eq. 1) or retention of configuration (eq. 2). Alternatively, the rearrangement could occur with prior ionization of the leaving group (S_N1 type) and subsequent loss of stereochemistry (eq. 3). It has been reported that hydride migration from boron proceeds with inversion of stereochemistry at carbon [3].

Propargyl chlorides [4] or acetates [5] may be converted into allenes via organoboranes. The postulated mechanism looks like a S_N2' reaction (eq. 4—7). Since optically-active propargyl acetates are readily available, the reaction represents a good method for monitoring the stereochemistry of the rearrangement with respect to the leaving group.

(*R*)-(+)-1-Octyn-3-ol acetate, $[\alpha]_D$ + 75.1° (neat) [6], prepared from the known (*R*)-(+)-alcohol [7] was treated in tetrahydrofuran with n-butyllithium at —120°C followed by tri-n-butylborane. Upon warming to room temperature

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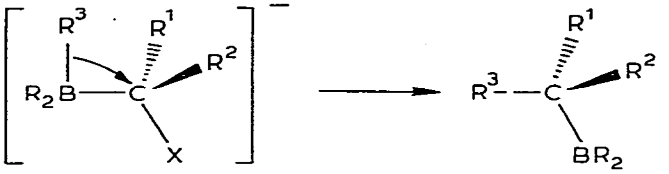
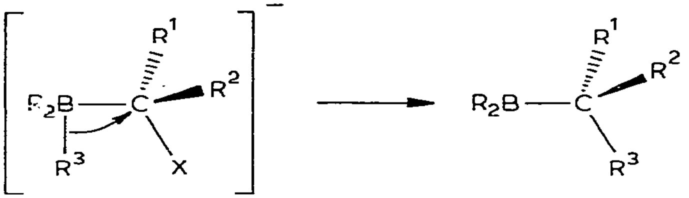
*This paper is dedicated to Professor H.C. Brown in recognition of his work in planting acorns along the borane trail [1].



(1)



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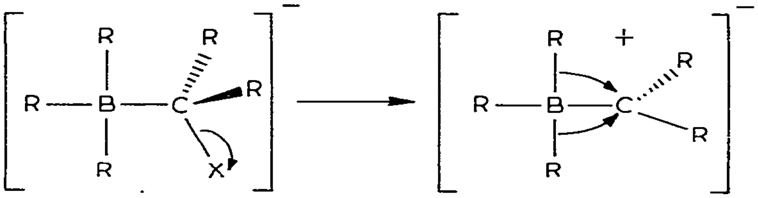
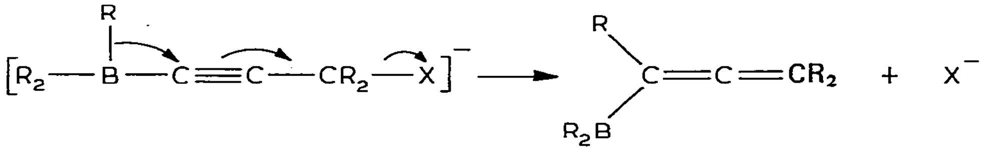


(3)

$$HC\equiv CCR_2X + n\text{-}BuLi \longrightarrow LiC\equiv CCR_2X \qquad (4)$$

$$LiC\equiv CCR_2X + R_3B \longrightarrow Li[R_3BC\equiv CCR_2X] \qquad (5)$$



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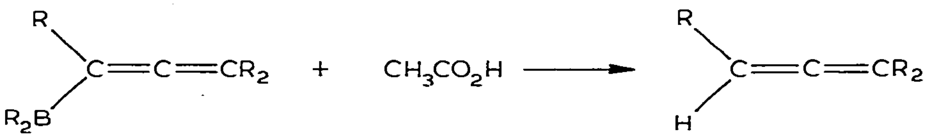
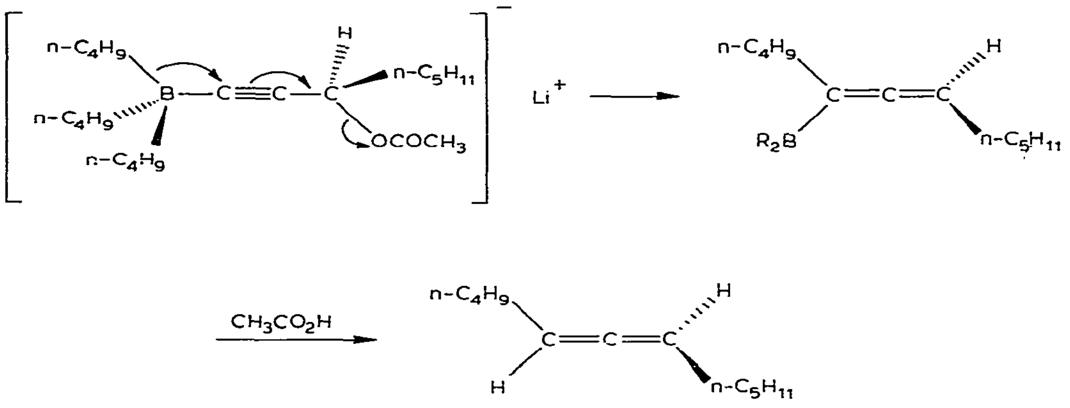


(7)

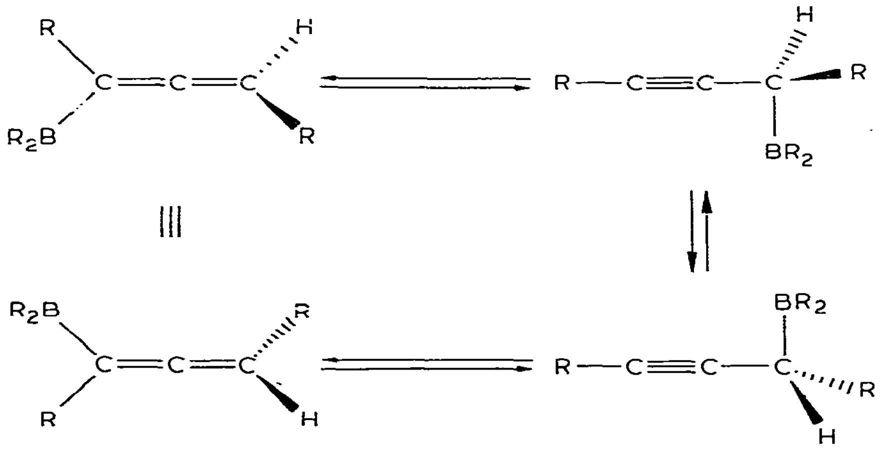
a precipitate formed. Protonation with acetic acid then produced 5,6-dodecadiene. (Protonation before the precipitate formed gave low yields of allene). Following basic-hydrogen peroxide oxidation, the allene along with approximately 10% of 5-dodecyne was isolated in 80% combined yield by column chromatography on silica gel. The allene had a specific rotation of $[\alpha]_D$ + 12.90° (neat) (14.33° corrected for the acetylene impurity). The allene is assigned the *S* configuration based on the Brewster—Lowe rule [8]. The alkyl group from boron thus migrates preferentially in an *anti*-relationship to the acetate (eq. 8). The allenic borane resembles a vinylborane and as such would be protonated by acetic acid with retention of configuration [9]. .



(8)

The maximum rotation for the allene is not known. Using the assumption based on Brewster's model of optical activity that all simple allenes have a similar molecular rotation and a value of 100° for the molecular rotation of 3,4-heptadiene [10], we estimate that our allene is 23% optically pure. Attempts to increase the rotation by changing the leaving group have so far failed. However, diethyl ether solvent increases the optical purity to 40%.

The allenic borane appears to be configurationally unstable at room temperature. A sample stirred overnight produced the allene, now contaminated with 28% of the acetylene, in a combined yield of 70%. The rotation was reduced to $[\alpha]_D$ + 1.22° (1.69° corrected for the acetylene impurity). The allenic borane may undergo a 1,3-boron shift similar to the allylic boranes [11] (eq. 9). However, such a rearrangement would have to occur with inversion on the allenic system since migration-rotation-migration gives back allene of the same absolute configuration. Another explanation may be that boron is lowering the energy barrier for isomerization around the double bonds of the allene.



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Acknowledgement

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