

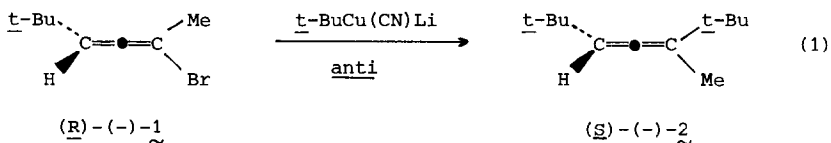
ON THE STEREOCHEMISTRY OF AN ALKYL CUPRATE INDUCED
 CONVERSION OF A BROMOALLENE INTO AN ALKYLALLENE

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Summary: By preparing levorotatory **2** following a route of known stereochemistry, we were able to elucidate the stereochemistry of the conversion of the levorotatory bromoallene **1** into levorotatory **2** by $t\text{-Bu}(\text{CN})\text{CuLi}$: the reaction occurs with retention of configuration in the allenyl moiety.

The elucidation of the stereochemistry of organometal mediated substitution reactions of propargylic and allenic substrates is an important research theme in our laboratories.¹ It has now been well established that cuprate mediated formations of allenes from propargylic precursors proceed with anti stereoselectivity.^{1a,b,2} Also allenic substrates may undergo S_N2' displacement reactions upon treatment with organocuprates.^{3,4} The products are then alkynes. In this connection, anti stereochemistry has been found for the conversion of bromoallenes into alkylacetylenes by various cuprates.⁴

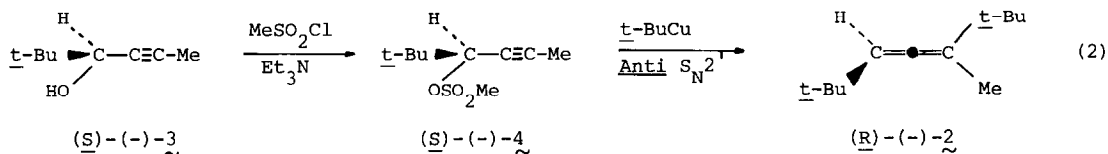
In a number of cases, it appeared that bromoallenes react with organocopper(I) species to give allenes.⁴⁻⁶ Until recently, the stereochemistry of such conversions was unknown, although it was tentatively assumed that retention of configuration in the allenyl moiety would be involved.⁵ However, in a very recent report⁴ it was stated that the following conversion occurs with inversion of configuration in the allenyl unit.



The anti stereochemistry was based on the basis of Lowe-Brewster rules which predict the S-configuration for (-)-**2**.⁴ From other work it is known that the rules are reliable for di-substituted allenes but not for tri-substituted allenes.^{1b,7} Allene **2** belongs to the latter category. It will be shown here that the rules indeed do not apply to **2**.

To determine the absolute configuration of (-)-**2**, it was prepared via an independent route of known stereochemistry. This route is outlined in eqn. (2). It involves the following steps. Alcohol (S)-(-)-**3** (57% ee)⁸ was converted into its mesylate (S)-(-)-**4** by treatment with MeSO_2Cl and Et_3N . Addition of **4**, at -50°C , in THF, followed by removal of the cooling bath and allowing

the temperature to rise to 20°C, gave almost pure levorotatory 2 (crude yield, ≈ 90%; purity > 99% after purification by g.l.c.; $[\alpha]_D^{20}$ -26.8° (n-pentane)). In view of the fact that organocopper(I)-induced S_N2' reactions in propargylic esters occur anti (vide supra), levorotatory 2 possesses the R absolute configuration.



The R absolute configuration for (-)-2 is also predicted by the so-called "chirality functions approach" developed by Ruch and Runge.¹⁰ The t-Bu(CN)CuLi-induced conversion of (R)-(-)-1 into (-)-2 (see eqn. 1) therefore proceeds with retention in the allenyl moiety and not with inversion, which confirms the early prediction by Landor et al. (cf⁵).

References and notes

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- The $[\alpha]_D$ -value refers to the purified allene.
- For instance, see: W. Runge in S. Patai (Ed.), "The Chemistry of Ketenes, Allenes, and Related Compounds"; Wiley: Chichester, 1980, Chapter 3.

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