The Asymmetric Synthesis and Absolute Configuration of Allenic Alcohols

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LANDOR, MILLER, and TATCHELL[1] recently reported that ketones could not be asymmetrically reduced to alcohols with lithium dimenthoxyaluminium hydride but accomplished this by using cyclic

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[1] S. R. Landor, B. J. Miller, and A. R. Tatchell, *Proc. Chem. Soc.*, 1964, 227.

aluminium hydride sugar complexes. Concurrent work had shown that enynols can readily be converted into optically active allenic alcohols with lithium dimenthoxyaluminium hydride and that the absolute configuration of the allene may be predicted by the following rule. The thermodynamically more stable cyclic allene complex predominates as shown in the preferred conformation which on hydrolysis gives *S*-(+)-allenic alcohol. Thus hex- and hept-2-en-4-yn-1-ol gave, with lithium dimenthoxyaluminium hydride, hexa-3,4-dienol $[\alpha]_D^{20}$ + 8·3° and hepta-3,4-dienol $[\alpha]_D^{20}$ + 2·3° respectively. Although we believe that the somewhat strained seven-membered allene complex is a possible intermediate (see Figure 1) the alternative polymeric allene aluminium menthylate complex is in no way excluded and models show that it would lead to the same steric results. The cyclic form is, however, pictorially much more convenient and is therefore preferred for formal presentation (Figure 1).

The absolute configuration of (+)-hexa-3,4-dienol was confirmed as *S* by heating (−)-α-chloroethyl but-1-yn-3-yl ether, $[\alpha]_D^{20}$ −44·5° (prepared from acetaldehyde, boron trichloride,[2] and *S*-(−)-but-1-yn-3-ol,[3] $[\alpha]_D^{20}$ −5·3°) at 200° in an electrically-heated tube filled with glass wool.[4] The unstable allenic aldehyde was reduced without isolation in the presence of lithium aluminium hydride to (+)-hexa-3,4-dienol, $[\alpha]_D^{20}$ + 5·3°, (Figure 2); (+)-hexa-3,4-dienol therefore has the *S*-configuration. The same principles are at present being applied to the elucidation of the absolute configuration of naturally occurring allenes.

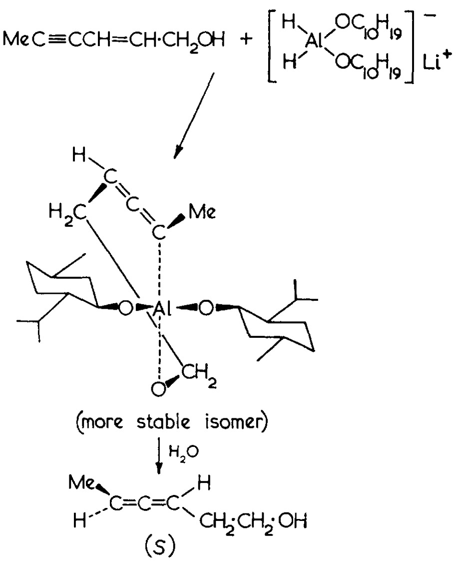

FIGURE 1

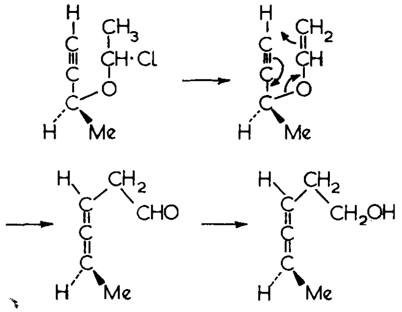

FIGURE 2

(*Received, July 19th,* 1965; *Com.* 454.)

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[2] D. K. Black and S. R. Landor, The preparation of α-chloroalkyl and vinyl ethers, *J. Chem. Soc.*, in Press.

[3] E. R. H. Jones, J. D. Loder, and M. C. Whiting, *Proc. Chem. Soc.*, 1960, 180, reduced (−)-but-1-yn-3-ol to (+)-butan-2-ol of known absolute configuration; confirmed in our laboratories, *cf.* C. S. L. Baker, P. D. Landor, S. R. Landor, and A. N. Patel, *J. Chem. Soc.* 1965, 4348.

[4] D. K. Black and S. R. Landor, The Claisen–Cope rearrangements of propargyl vinyl systems, *J. Chem. Soc.*, in Press.