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The Asymmetric Reduction of Alkenynols with the Lithium Aluminium Hydride–3-*O*-Benzyl-1,2-*O*-cyclohexylidene-α-D-glucofuranose Complex and the Determination of the Absolute Configuration of Naturally Occurring Allenes

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IT has recently been shown[1] that optically active allenic alcohols may be obtained and their absolute configuration determined by reduction of alk-2-en-4-yn-1-ols with lithium dimenthoxyaluminium hydride. The configuration of the simple (+)-allenic alcohols, hexa-3,4-dien-1-ol and hepta-3,4-dien-1-ol, was shown to be (*S*) and this was substantiated by a Claisen type of rearrangement of (−)-but-1-yn-3-yl α-chloroethyl ether to give (*S*)-(−)-hexa-3,4-dien-1-ol *via* a six-membered, cyclic transition state. The same principle may be applied to the synthesis and determination of the absolute configuration of the naturally occurring optically active nona-3,4-dien-6,8-diyn-1-ol (marasin, $[\alpha]_D^{20} \pm 385°$)[2] and deca-3,4-dien-6,8-diyn-1-ol (9-methylmarasin, $[\alpha]_D^{20} + 340°$)[3] but the same reducing complex cannot be used as it is virtually impossible to separate traces of (−)-menthol from the products. We therefore investigated the use of lithium aluminium hydride–3-*O*-benzyl-1,2-*O*-cyclohexylidene-α-D-glucofuranose complex[4] for the asymmetric reduction of alk-2-en-4-yn-1-ols. Reduction of hex-2-en-4-yn-1-ol, hept-2-en-4-yn-1-ol, and non-2-en-4-yn-1-ol with the lithium aluminium hydride monosaccharide complex gave (−)-hexa-3,4-dien-1-ol, $[\alpha]_D^{20} - 10°$, (−)-hepta-3,4-dien-1-ol, $[\alpha]_D^{20} - 8{\cdot}9°$ and (−)-nona-3,4-dien-1-ol, $[\alpha]_D^{20} - 7{\cdot}4°$ all of the (*R*)-configuration (*cf.* ref. 1). The thermodynamically more stable transition state of the hydroxyallenealuminium–monosaccharide complex therefore has the (*R*)-configuration and this is borne out by an examination of models of the complex in the polymeric form which show that the (*R*)-isomer is sterically more favourable than the (*S*)-isomer. Extension of this method to the asymmetric synthesis of allenynes and allendiynes gave allenic alcohols with negative rotations and examination of models of these compounds suggests that the more stable form again has the (*R*)-configuration. Thus 8,8-dimethylnon-2-en-4,6-diyn-1-ol gave (−)-8,8-dimethylnona-3,4-dien-6-yn-1-ol, $[\alpha]_D^{25} - 12{\cdot}5°$, λ_{max} 219 mμ (ϵ 14,690), 7-phenylhept-2-en-4,6-diyn-1-ol gave 7-phenylhepta-3-4-dien-6-yn-1-ol, $[\alpha]_D^{25}$ $-3{\cdot}1°$, λ_{max} 205 (ϵ 41,500), 257 (ϵ 13,600), 273·5 (ϵ 19,300), 288 mμ (ϵ 14,800), λ_{sh} 218 mμ (ϵ 29,000), non-2-en-4,6,8-triyn-1-ol[5] gave (−)-marasin, $[\alpha]_D^{25} - 26{\cdot}6°$, λ_{max} 208 (ϵ 51,000), 224 (ϵ 3,200), 237 (ϵ 5,000), 249·5 (ϵ 8,900), 263 (ϵ 14,100), and 278 mμ (ϵ 12,500) (*cf.* ref. 2) ν_{max} 3330, 2220, and 1960 cm.$^{-1}$ and dec-2-en-4,6,8-triyn-1-ol[6] gave 9-methylmarasin, $[\alpha]_D^{25}$ $-11{\cdot}3°$, λ_{max} 208 (ϵ 56,000), 224·5 (ϵ 3,900), 237

(ϵ 6,500), 250·5 (ϵ 12,100), 264 (ϵ 16,000), and 280 mμ (ϵ 12,900).[3]

It follows therefore that (—)-marasin and (—)-9-methylmarasin should have the (*R*)-configuration and we believe this constitutes the first determination of the absolute configuration of a naturally occurring allene. An extension of Brewster's theory[7] predicted on the basis of polarisabilities of substituents that the system (*R*)-Me(H)C$\equiv$C·C$\equiv$C·CH$=$C$=$CH·CH_2·CH_2OH should have a negative rotation.[8] With the present determination of the absolute configuration of two such alcohols, marasin and 9-methylmarasin, it may be concluded with some confidence that other lævorotatory compounds in the same series have the (*R*)-configuration and dextrorotatory compounds the (*S*)-configuration.

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[1] R. J. D. Evans, S. R. Landor, and J. P. Regan, *Chem. Comm.*, 1965, 397.

[2] G. Benz, *Arkiv Kemi*, 1959, **14**, 305, 475; R. C. Cambie, A. Hirschberg, E. R. H. Jones, and G. Lowe, *J. Chem. Soc.*, 1963, 4120.

[3] R. E. Bew, J. R. Chapman, Sir Ewart R. H. Jones, B. E. Lowe, and G. Lowe, *J. Chem. Soc.* (*C*), 1966, 129.

[4] S. R. Landor, B. J. Miller, and A. R. Tatchell, *J. Chem. Soc.*, in the press; *cf. Proc. Chem. Soc.*, 1964, 227.

[5] S. R. Landor, E. S. Pepper, and J. P. Regan, *J. Chem. Soc.*, in the press. *cf.* E. R. H. Jones and J. S. Stephenson, *J. Chem. Soc.*, 1959, 2179; F. Bohlmann, P. Herbst, and H. Gleinig, *Chem. Ber.*, 1961, **94**, 948.

[6] S. Prevost, J. Meiser, W. Chodkiewiez, P. Cadiot, and A. Willemart, *Bull. Soc. chim. France*, 1961, 2171.

[7] J. H. Brewster, *J. Amer. Chem. Soc.*, 1959, **81**, 5475.

[8] G. Lowe, *Chem. Comm.*, 1965, 411.