

8 Synthesis highlights: a review of the literature for 1997

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1 Introduction

This year, almost more than any other in the recent past, has demonstrated the seemingly limitless ability (of certain research groups at least) to approach and complete the synthesis of complex structures. The synthesis of natural products, once an esoteric pastime whose main purpose was to act as a vehicle for the exemplification of synthetic methodology, has taken a different direction this year due mainly to the isolation in 1996 of the antitumour agents epothilone A, **1** and B, **2**. These macrocyclic lactones have elicited much attention from molecular biologists and synthetic chemists alike as they are able to stabilise tubulin formation in a manner similar to TaxolTM and have similar antitumour activities. Importantly however, the structurally less complex epothilones are potentially available by total synthesis unlike the more structurally elaborate and synthetically more challenging taxane system. A number of reports this year have been concerned with the total synthesis of these natural products, and combined with the renewed interest in the use of solid supports in organic synthesis, combinatorial techniques have been adopted in the synthesis of 'libraries' of analogues, which have generated compounds which are more potent than the natural products themselves.^{1b,c}

2 Total synthesis of epothilones A and B

Preamble

Any approach to the synthesis^{1a} of epothilone A, **1**, has to address a number of key issues including the introduction of seven chiral centres, a *cis*-epoxide moiety, two hydroxy groups, two secondary methyl groups, one *gem*-dimethyl group, a trisubstituted double bond and of course the construction of the 16-membered ring itself. An obvious disconnection for the lactone ring would be to synthesise the corresponding hydroxy acid **3**, which hopefully could be cyclised using standard methodology (Scheme 1). Common to all the approaches disclosed to date is the introduction of the epoxide moiety at a late stage in the synthesis: the realisation of such a strategy relies upon the chemoselective epoxidation of the more exposed face of the less sterically congested double C₁₂-C₁₃ bond rather than epoxidation at C₁₆-C₁₇ or indeed oxidation of the thiazole ring. A more subtle question is concerned with the

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