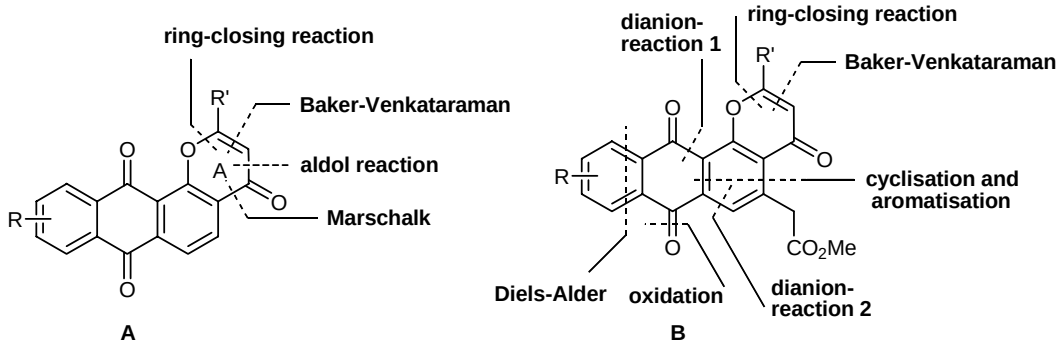
Synthesis of 4*H*-Anthra[1,2-*b*]pyrane-Antibiotics
Total Synthesis of Premithramycinone H

The 4*H*-anthra[1,2-*b*]pyrane antibiotics are known for their antibacterial and antitumor activity. In addition, the remarkable antitumor activity of premithramycinone H was described in a recent report. The goal was to make this class of compounds easily available. The key steps of the first approach (**A**) included a Marschalk alkylation of hydroxylated anthraquinones followed by Baker-Venkataraman chain elongation and subsequent acid catalysed cyclisation of ring A. The second approach (**B**) started with a Diels-Alder reaction between allene diester and ketene acetals followed by two successive condensations of the dianions of acetoacetate and 2,4-pentanedione and the monoester. The synthesis was finished by oxidation, Baker-Venkataraman rearrangement and internal ring closing reaction. Cleavage of the methyl ethers afforded the natural product premithramycinone H. One of the synthesised compounds showed a significant inhibition of growth of human tumor cells.



In addition, the catalytic oxidation of hydroquinones to quinones with ammonium cerium nitrate (CAN) was investigated. The use of *tert*-butyl hydroperoxide (TBHP) to reoxidize the cerium provided very good results. With this method it was possible to oxidise mono methyl ethers in good yield as well.