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Efficient Entry to the Steroidal 14α-Methyl-8-ene System

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The 14α-methyl-8-ene steroids are important intermediates of sterol biosynthesis, but their efficient chemical preparation has not been reported before. In a continuing study of the acid-catalyzed reaction of steroidal epoxide, the pivalyl ester of 14α,15α-epoxy-5-cholesten-3β-ol has now been treated with boron trifluoride etherate in benzene to give the 8-en-15α-ol in 75% yield. Oxidation of this alcohol with pyridinium chlorochromate gave, in 73% yield, the corresponding 15-ketone which exhibited a strongly negative Cotton effect indicating the 14β-H cofiguration. The 15-ketone was methylated with methyl iodide/potassium *tert*-butoxide in *tert*-butanol to afford the 14α-methyl-15-ketone in 73% yield. Subsequent deoxygenation by Huang-Minlon reduction afforded the final product 14α-methylcholest-8-en-3β-ol.

The above mentioned procedures were applied to 4,4-dimethyl analog to yield 24,25-dihydrolanosterol identical with natural product.

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