

Title	Efficient entry to the steroidal 14 α -methyl-8-ene system
Sub Title	
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Publisher	共立薬科大学
Publication year	1990
Jtitle	共立薬科大学研究年報 (The annual report of the Kyoritsu College of Pharmacy). No.35 (1990.) ,p.77- 77
JaLC DOI	
Abstract	
Notes	抄録
Genre	Technical Report
URL	https://koara.lib.keio.ac.jp/xoonips/modules/xoonips/detail.php?koara_id=AN00062898-00000035-0077

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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 steroid epoxide, the pivalyl ester of $14\alpha,15\alpha$ -epoxy-5-cholest-3 β -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 configuration. 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.

* 本報告は *Chem. Pharm. Bull.*, 38, 1796—1797 (1990) に発表。