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THE CONVERSION OF STEROIDAL LACTONES TO ORTHO ESTERS

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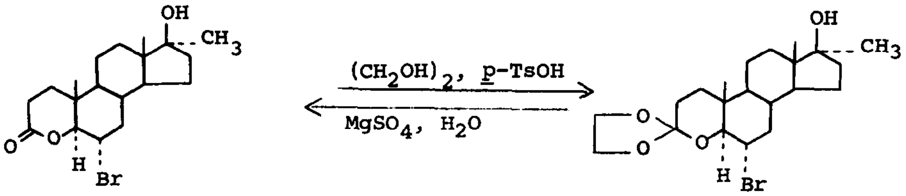
The conversion of lactones to ortho esters has been accomplished by treatment with epoxides in the presence of boron trifluoride (1) or with triethyloxonium fluoroborate followed by sodium ethoxide. (2) We have recently found that ketalization of steroidal ketones containing a lactone group also resulted in reaction of the lactone with ethylene glycol. The resultant ortho esters are readily cleaved to the starting lactones.

A mixture of 1, (3) ethylene glycol and a catalytic amount of p-toluenesulfonic acid in benzene solution was refluxed for 66 hours with continuous removal of water to afford 2 (4) (72% yield): mp 195-197°; nmr ($CDCl_3$) δ 3.9-4.3 (m, 4H), mass spectrum (low resolution) m/e 428 (M^+). The infrared spectrum of 2 exhibited no carbonyl band.

Treatment of 3 (5) under the above conditions gave 4 (56% yield): mp 163-164°; nmr ($CDCl_3$) δ 3.8-4.2 (m, 4H), mass spectrum (low resolution) m/e 350 (M^+).

Cleavage of the ortho esters 2 and 4 to the starting lactones proceeded readily using anhydrous magnesium sulfate in wet benzene as described (6) for the cleavage of Δ^4-3-ethyleneketals.

Steric hindrance is apparently crucial in the ortho ester formation since 17α-oxo-D-homo-1,4-androstadiene-3,17-dione (7) did not react with ethylene glycol under the above conditions. Monocyclic lactones such as γ-butyrolactone are opened under the reaction conditions and do not give ortho esters.



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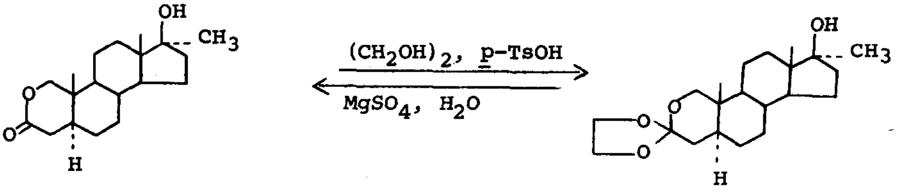

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