

ABSTRACT

SOME REACTIONS OF Δ^5 -STEROIDS

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This thesis documents results from a study of some reactions of Δ^5 -steroids. The reactions were examined primarily in an attempt to establish their scope and limitations.

Chapter 1 is a brief review of the reactions of steroidal and simple olefins with mercury(II) salts.

In Chapter 2 the reaction of Δ^5 -steroids with mercury(II) trifluoroacetate (Treibs oxidation) was investigated. The effect of substrate structure, in particular the variation of substituents at C-3, was examined. The mechanism of the reaction was also studied.

Chapter 3 examines the effect of varying the reaction conditions that were used in Chapter 2 with a view to optimizing them. During the variation of metal salts a novel palladium(II) trifluoroacetate-steroid complex was isolated.

Substituent effects in the allylic acetoxylation of the steroidal olefins with bromine and silver acetate-pyridine were studied in Chapter 4. The intramolecular reactions of some of these substituents are highlighted.

Appendix A discusses briefly the acetolysis of 3 β -acyloxy-6 β -hydroxyandrost-4-en-17-ones, the reaction of 6 β -hydroxy-3 α ,5 α -cycloandrostan-17-one with bromine and silver acetate in chloroform, and the

reactions of steroidal diol monoacetates with methane- and toluene-p-sulfonyl chloride.

Appendix B contains X-ray crystallographic data for a number of products of the reactions studied.