STUDIES ON THE OXIDATION OF AROMATIC STEROIDS

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T.D.R. Manning

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TABLE OF CONTENTS

	Page
ABSTRACT	iii
INTRODUCTION	1
Chromium(VI) Oxidation of Saturated Carbon-Hydrogen Bonds	3
Chromium(VI) Oxidation at Carbon-Carbon Double Bonds	18
Chromium(VI) Oxidation of Alcohols	21
Chromium(VI) Oxidation of Aldehydes	24
Chromic Acid Oxidation of Aromatic Steroids	25
Chromic Acid Oxidation of Ring-C Aromatic Diterpenoids	27
DISCUSSION	
PART A	
Synthesis of the aromatic steroids which were to be oxidised in this study	32
PART B	
Chromic acid oxidation of ring-A aromatic steroids	46
Chromic acid oxidation of a ring-B, and a ring-C aromatic steroid	73
EXPERIMENTAL	81
REFERENCES	143
DIAGRAMS	155
ACKNOWLEDGEMENTS	168

ABSTRACT

This thesis is concerned primarily with a study of the oxidation of aromatic steroids employing either chromium trioxide-aqueous acetic acid or chromium trioxide-aqueous sulphuric acid-acetone mixtures.

The nature of the chromic acid oxidation of various functional groups is discussed first and this is followed by an outline of the methods used for the synthesis of the aromatic steroids which were oxidised in this study. The second part of the discussion deals with the oxidation of these aromatic steroids.

It was found that chromic acid oxidation of ring-A aromatic steroids containing a strong electron-donating C_3-substituent, such as methoxyl, gave the corresponding 9-hydroxy-11-oxo derivative (ketol). However, a ketol was not formed if a C_3-methoxyl substituted ring-A aromatic steroid also contained a substituent at C_1.

When a C_3-methoxyl substituent was present, the 6-oxo-ring-A aromatic steroid was a minor oxidation product but such compounds were the major products from the chromic acid oxidation of ring-A aromatic steroids containing a weak C_3-electron-donating group, such as acetoxyl. The oxidation of a ring-A aromatic steroid containing a C_2-methoxyl substituent gave an almost quantitative yield of the corresponding 6-oxo compound.

Suzuki[103] has claimed that the major oxidation product of 17β-acetoxy-3-methoxyestra-1,3,5(10)-triene (34b) is 17β-acetoxy-9α-

hydroxy-3-methoxyestra-1,3,5(10)-trien-11-one (123). Physical and chemical evidence are presented to show that this product is in fact the 9β-hydroxy epimer and a reaction pathway for its formation is proposed.

An examination of the oxidation products of a ring-B aromatic steroid and a ring-C aromatic steroid showed that no ketols were formed.