

APPLICATIONS OF CHROMOUS CHLORIDE - I

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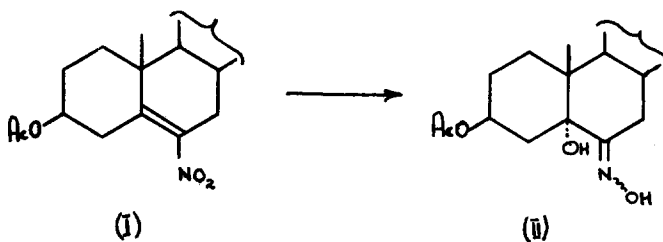
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The reductive hydrolysis of 6-nitrocholesteryl acetate (I) with zinc and acetic acid is a standard method^{1,2} for the preparation of 6-ketocholesteryl acetate. Chromous chloride or its acetate forms a convenient reducing agent which has had recent application³ in the steroid field. Treatment of 6-nitrocholesteryl acetate (I) with eight equivalents of 0.1N chromous chloride [standardized potentiometrically⁴] for 3 hours under nitrogen in refluxing tetrahydrofuran gave, in 80% yield the oxime (II) of 3 β -acetoxy-5 α -hydroxy-6-ketocholestane [m.p. 146-150°]. This was identified by its spectral properties and by comparison with a sample prepared from 3 β -acetoxy-5 α -hydroxy-6-ketocholestane. This novel hydroxylation and reduction appears to afford a synthesis of α -hydroxy-oximinosteroids and hence α -hydroxy-amino-steroids⁵. Its scope and stereochemical consequences

are under investigation with this and other nitro systems.

In a recent note it has been stated⁶ that catalytic reduction of nitro-olefins can under certain circumstances give rise inter alia, to α -hydroxyoximes.



During the preparation of the oxime using the standard pyridine:hydroxylamine hydrochloride procedure, at room temperature, it was found that some hydrolysis of the 3β -acetate occurred. This gave rise to a mixture of the oximes of 3β -hydroxy [m.p. $227-229^\circ$] and 3β -acetoxy- 5α -hydroxy-6-ketocholestanes [m.p. $146-150^\circ$] which accounts for the discrepancy in physical constants found for this compound in the literature [lit.⁷ m.p. $204-206^\circ$].

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