

STEROIDS XII* A NOVEL ADDITION REACTION OF MERCURIC SALTS
WITH UNSATURATED STEROIDAL KETONES

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In the course of our studies on the reactivity of steroidal 3-keto-1,4,6-trienes¹ we attempted to carry out their oxidation² by means of mercuric salts. Mercuric acetate and 17 α -methyl-androsta-1,4,6-triene-17 β -ol-3-one in glacial acetic acid gave a new polar product, which, however, could not be isolated from the reaction mixture. After adding sodium chloride solution we were able to isolate a relatively readily crystallizing product m.p. 155-162^o, to which we ascribed structure 2a, i.e. 17 α -methyl-2-chloromercuri-androsta-1,4,6-triene-17 β -ol-3-one, on the basis of spectral data.

The UV spectrum of compound 2a is very similar to that of steroidal 3-keto-1,4,6-trienes³ (λ_{max} = 207, 267, and 303 nm). The IR band at ν = 1706 cm⁻¹, corresponding to unsaturated carbonyl of the keto group, is considerably displaced, and other bands at ν = 1612, 1579, and 3500 cm⁻¹ are characteristic for this system.

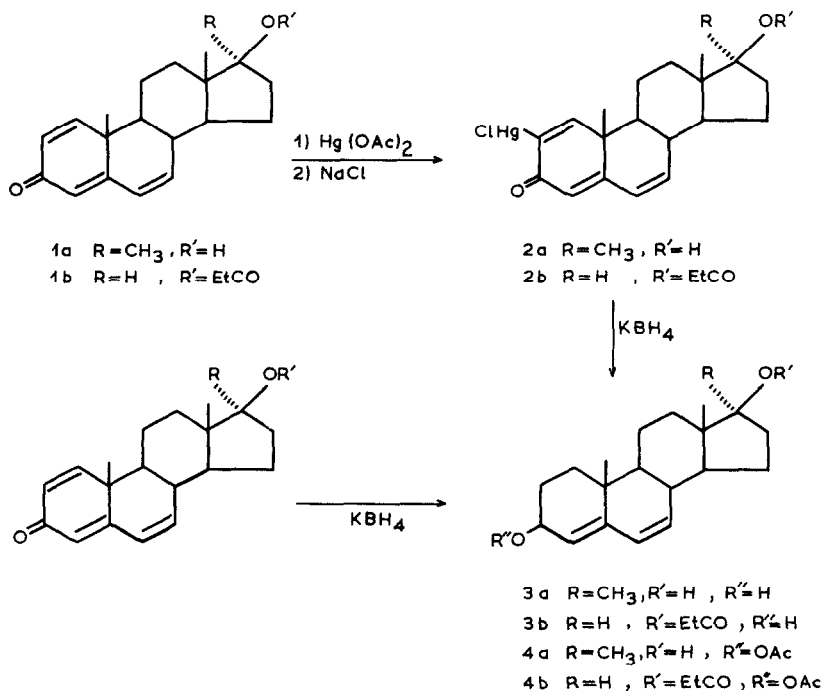
NMR spectrum of compound 2a indicates the presence of isolated vinyl proton at C₁ (2.62 τ), and a system of three conjugated vinyl protons at C₄ (3.98 τ), C₆ (3.95 τ), and C₇ (3.75 τ). The remaining part of the spectrum contains signals of methyl groups characteristic for other 17-methyl steroids C₁₈ (9.12 τ), C₁₉ (8.90 τ), and C₂₀ (8.83 τ).

The mass spectrum contains molecular peak corresponding to C₂₀H₂₅O₂HgCl (2a) and peaks of the ions Hg⁺⁺ and HgCl⁺.

The chemical proof of the structure of compound 2a consists of the reduction with potassium borohydride to the known 17 α -methyl-androsta-4,6-diene-

* For Part XI see reference 1.

-3 β ,17 β -diol (3a) m.p. 230-232 $^{\circ}$. The UV spectrum of compound 3a has maxima at 232, 240 and 248 nm; its IR spectrum has a broad band at 3250-3500 cm^{-1} corresponding to OH groups, and a band at 1660-1636 cm^{-1} corresponding to $>\text{C}=\text{C}<$ group.



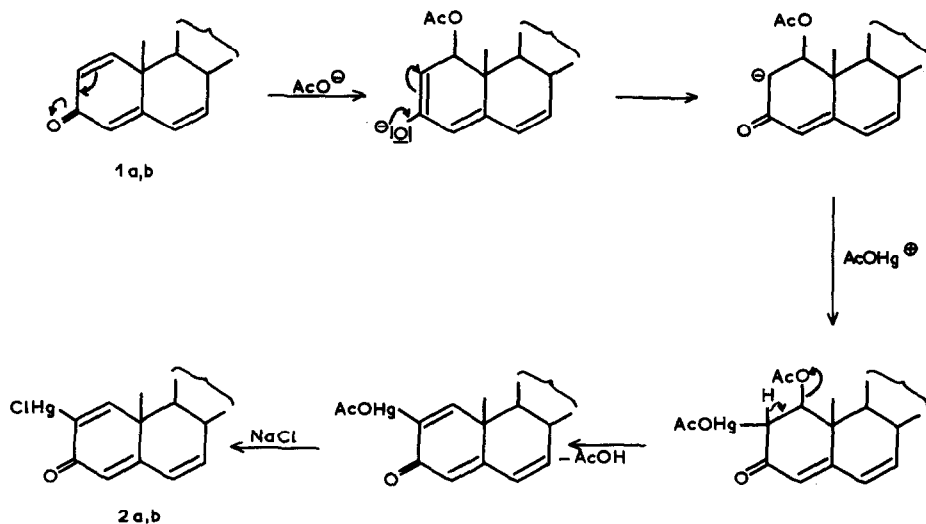
Scheme 1.

We have also prepared the same compound 3a from 17 α -methyl-androsta-1,4,6-triene-17 β -ol-3-one by means of sodium borohydride reduction. The steps 1b \rightarrow 3b were analogous when androsta-1,4,6-triene-17 β -ol-3-one propionate was used as the starting material.

Compound 2b melts at 173.5-175 $^{\circ}$; its UV spectrum has maxima at 217, 269, and 303 nm. It was reduced with potassium borohydride to compound 3b m.p. 135-137 $^{\circ}$. Compounds 2a and 2b could not be prepared by direct action of mercur-

ic chloride on compounds 1a and 1b.

The mechanism of addition of mercuric acetate probably consists of the attack by AcO^- ion on polarized β -keto-1,4,6-triene system, followed by addition of $\text{Hg}(\text{OAc})^+$ ion to the resulting carbanion bearing the negative charge on the second carbon, and formation of $\text{C}_1\text{-C}_2$ double bond by the loss of acetic acid elements.



Scheme 2.

We are very much indebted to Dr. H. W. Fehlhaber (University of Bonn) for measuring the MS of 17α -methyl-2-chloromercuri-androsta-1,4,6-triene- 17β -ol-3-one.

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