Unusual Mercury(II) Acetate Oxidation of Steroidal Alkenes

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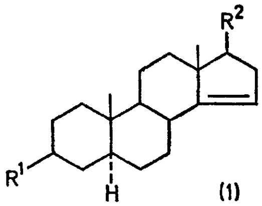
Summary Reaction of mercury(II) acetate with di- and tri-substituted double bonds of certain steroids led to the formation of αβ-unsaturated ketones.

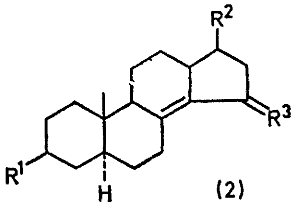
In connection with a programme leading to the synthesis of steroidal αβ-unsaturated ketones of the 14-en-16-one type, we have investigated the reaction of mercury(II) acetate (Treibs reaction)[1] with 14-enes (**1**). Reaction of 2 equivs. of mercury(II) acetate with either 5α-ergost-14-ene (**1a**), 3β-hydroxy-5α-ergost-14-ene acetate (**1b**), 3β-hydroxy-5α-cholest-14-ene acetate (**1c**) did not yield the expected 16ξ-acetoxy-14-ene, but in all cases the major product‡ was the 8(14)-en-15-one (**2a**, **2b**, and **2c** respectively).§ Other unsaturated ketones could not be detected in the reaction mixture. The tetra-substituted double bond of cholest-8(14)-ene (**2d**) was unreactive toward mercury(II) acetate under these conditions.

The investigation was extended to a system where a variety of possible products could be formed, such as 5α-cholest-2-ene (**3**). Reaction of (**3**) with 2 equivs. of mercury(II) acetate under reflux in 45% chloroform–acetic acid in an atmosphere of nitrogen precipitated mercury(I) acetate 0·5 h. Examination of the reaction mixture by t.l.c. indicated no significant products in this time period. Continued reaction for a total of 66 h gave, after extensive chromatography, 20% yield of 5α-cholest-1-en-3-one (**4**) with 70% recovery of starting material.



(1)

	R^1	R^2
(a)	H	C_9H_{19}
(b)	OCOMe	C_9H_{19}
(c)	OCOMe	C_8H_{17}



(2)

	R^1	R^2	R^3
(a)	H	C_9H_{19}	O
(b)	OCOMe	C_9H_{19}	O
(c)	OCOMe	C_8H_{17}	O
(d)	H	C_8H_{17}	H_2

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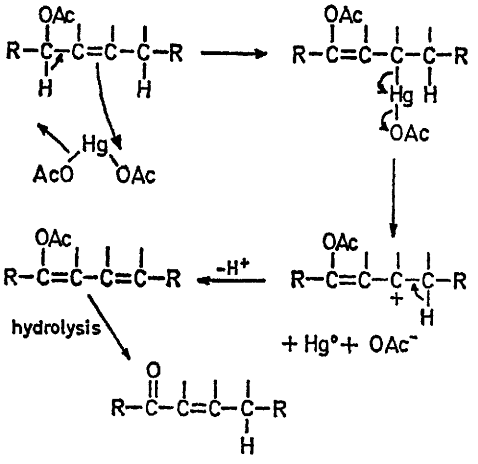
‡ Considerable starting material was recovered (30—50%) with a yield of 10% of the unsaturated ketone.

§ Products are identified by mass, i.r., u.v., and n.m.r. spectra and by comparison with authentic samples by means of thin layer chromatography (t.l.c.) and mixed m.p.



SCHEME

A mechanism for the normal mercury(II) acetate oxidation implicates the formation of allylic mercuriacetates[2] as intermediates. Our findings indicate an oxidation step additional to the normal mechanisms. A possible mechanism for the formation of the unsaturated ketone starting from a normal product, an allylic acetate, is indicated in the Scheme.

If the scheme is applicable, the intermediate allylic acetate must have the same structure as the unsaturated ketone formed, and the unsaturated enol acetate must undergo hydrolysis in the workup of the reaction mixture. Treibs[1a,3] has demonstrated that certain ketones react with mercury(II) acetate at high temperature to produce α-acetoxy ketones. Presumably these reactions proceed through the intermediacy of enol-acetates. Halpern and his co-workers[4] have shown mercury(II) catalysis of the hydrolysis of enol esters to the corresponding ketones.

Work is in progress on the scope, kinetics, and mechanism of the abnormal reaction.

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[2] Z. Rappaport, S. Winstein, and W. Young, *J. Amer. Chem. Soc.*, 1972, **94**, 2320, and references therein.

[3] W. Treibs, *Naturwiss.*, 1948, **35**, 125.

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