Mechanism of Formation of Steroidal Dithians: a Simple Analogy

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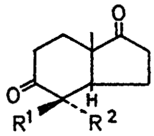
Summary A mechanism for the formation of the tricyclic dithian (VII) is suggested, and the possible formation of steroidal dithians in a similar manner is noted.

THE preparation of steroidal dithians[1,2] has recently been the subject of discussion,[3] and the mechanism of formation previously suggested[1] has been questioned. We here report a rearrangement that is pertinent to these discussions.

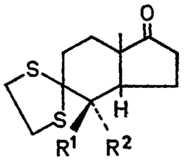
Condensation of an epimeric mixture of *cis*-hydroxydiones (I, II)[4] with 1 equiv. of ethanedithiol in the presence of boron trifluoride etherate resulted in the formation of two ethylene dithioacetals (III) and (IV) which were separated by alumina chromatography to give (III) as a colourless oil, and (IV) as colourless microcrystals, m.p. 126—128°. The n.m.r. spectrum of (III) indicated the presence of an angular methyl group [τ 8·98 (s, 3H)], an ethylene dithioacetal group [τ 6·72 (s, 4H)], and a proton at C-5 which was coupled with the angular proton at C-6 [τ 6·22 (d, 1H) J 3·5 Hz] (ν_{max} 1730 cm.$^{-1}$). The n.m.r. spectrum of (IV) indicated the presence of an angular methyl group [τ 8·98 (s, 3H)], and an ethylene dithioacetal group [τ 6·68 (s, 4H)], although the resonance due to the proton at C-5 was obscured by the dithioacetal resonance. (ν_{max} 1730 cm.$^{-1}$). Confirmation of the structures assigned to (III) and (IV) was obtained by desulphurisation using Raney nickel catalyst which yielded the hydroxyketone (V). Oxidation of (V) gave the known[5] *cis*-dione (VI).

Elution of (III) and (IV) through a silica column with chloroform resulted in the formation in high yield (80%) of a rearrangement product, $C_{12}H_{16}OS_2$, b.p. 155°/0·35 mm., (ν_{max} 1735 cm.$^{-1}$). The n.m.r. spectrum indicated the presence of an angular methyl group [τ 8·92 (s, 3H)], nine aliphatic protons [τ 7·5—8·8 (m, 9H)], and an ethylene dithioacetal group [τ 6·81 (s, 4H)], thus leading to the structure (VII) for this product. Confirmation of this structure was provided by desulphurisation using active

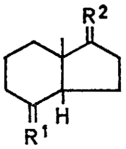
Raney nickel catalyst which also caused hydrogenation and the formation of the alcohol (VIII). Oxidation of (VIII) using Jones' reagent[6] gave the known[7] *cis*-ketone (IX). The above rearrangement was also accomplished by treatment of (III) and (IV) with boron trifluoride etherate and acetic acid when the product (VII) was obtained in high yield (82%).



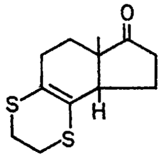
(I) R^1 = H, R^2 = OH
(II) R^1 = OH, R^2 = H



(III) R^1 = H, R^2 = OH
(IV) R^1 = OH, R^2 = H

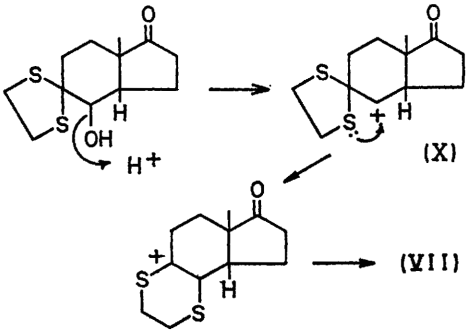


(V) R^1 = H,OH, R^2 = O
(VI) R^1 = R^2 = O
(VIII) R^1 = H,H, R^2 = H,OH
(IX) R^1 = H,H, R^2 = O



(VII)

A possible mechanism for the formation of (VII) is indicated (see Scheme). Clearly the formation of a carbonium ion of type (X) and its subsequent rearrangement could explain the formation of steroidal dithians[1] under reaction conditions similar to those described herein.



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(*Received, October* 10*th*, 1969; *Com.* 1531.)

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