

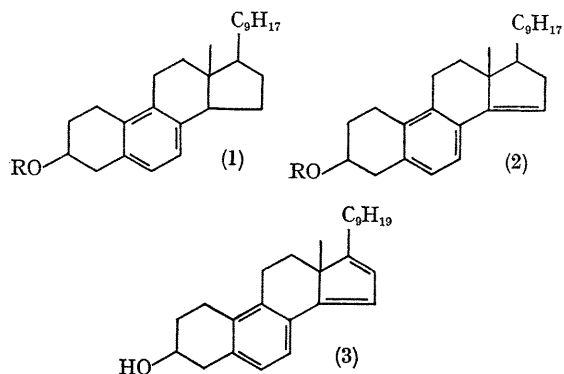
Stereoelectronic Effects in the Dehydrogenation of Neoergosterols

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Summary Neoergosterols are rapidly oxidised to their 14-dehydro-derivatives by dichlorodicyanobenzoquinone at room temperature.

ALTHOUGH various classes of compounds, including phenols, enol ethers, and benzyl alcohols, react rapidly with 2,3-dichloro-5,6-dicyanobenzoquinone at room temperature,¹ there are few examples of the rapid oxidation of hydro-aromatic compounds not activated by oxygen functions.² We now find that neoergosterol (1; R = H) reacts rapidly at room temperature with dichlorodicyanobenzoquinone to give exclusively the 14-dehydro-derivative (2; R = H). The reaction was carried out in benzene or dioxan, using equimolar amounts of steroid and quinone, and the styrene (2; R = H), m.p. 178—179°, was obtained in 80% yield.†



A similar reaction occurs with neoergosterol acetate (1; R = Ac) to give the styrene (2; R = Ac), m.p. 154—155°, in 86% yield. Formation of 14-dehydro-derivatives from the corresponding 22,23-dihydronoergosterols,³ in 87—90% yield, confirms that hydride abstraction takes place exclusively at C-14. Further dehydrogenation of the alcohol at room temperature also occurs in ring D, and the $\Delta^{14,16}$ -derivative (3) is formed. Introduction of the second double bond takes place much more slowly.

The remarkable ease and specificity of these dehydrogenations are mainly a result of the tertiary benzylic hydrogen at C-14 being almost perpendicular to the plane of the aromatic ring, thereby allowing maximal σ - π overlap in the transition state for hydride abstraction. However, the complete absence of attack at the activated tertiary hydrogens in the side-chain (at C-20 and C-24) suggests that a further factor augments the stereoelectronic effect. This is preferential π -complexing between the aromatic nucleus and the high-potential quinone.^{1,4} On mixing the reactants in benzene or dioxan, the solution initially appears dark; the colour lightens rapidly as reaction proceeds and hydroquinone is precipitated. The specificity of the oxidation is understandable if π -complexing is the controlling factor, allowing ready abstraction of the tertiary hydride ion at C-14. Proton transfer from the carbonium ion to the hydroquinone anion can then occur before separation of the observed products. Attempts to determine whether π -complex formation is the rate determining step in this sequence are in hand.

(Received, June 12th, 1969; Com. 845.)

† All new components gave elemental analyses and spectroscopic data in agreement with the structures shown. Yields quoted are on recrystallised products.

¹ D. Walker and J. D. Hiebert *Chem. Rev.*, 1967, **67**, 153.

² M. Heller, R. H. Lenhard, and S. Bernstein, *Steroids*, 1967, **10**, 211.

³ E. L. McGinnis, G. D. Meakins, and D. J. Morris, *J. Chem. Soc. (C)*, 1967, 1238.

⁴ L. M. Jackman, *Adv. Org. Chem.*, 1960, **2**, 329; cf. J. W. A. Findlay and A. B. Turner, *J. Chem. Soc. (C)*, submitted for publication.