Adducts Derived from Steroidal-5,7-dienes and 4-Phenyl-1,2,4triazoline-3,5-dione: a Route to Steroidal 8(14)- and 14(15)-enes

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Summary The acid-catalysed decomposition of adducts derived from various steroidal-5,7-dienes and 4-phenyl-1,2,4-triazoline-3,5-dione furnishes novel routes to unsaturated steroids containing inter alia the 8(14)- or 14(15)-ene function.

In continuation of our investigations of adducts derived from steroidal-5,7-dienes and 4-phenyl-1,2,4-triazoline-3,5dione we now report reactions which furnish various 8(14)or 15(15)-enes from certain adducts.

Thus, interaction of 4,4-dimethylcholesta-5,7-diene-3-one, in dichloromethane, at room temperature, with 4-phenyl-1,2,4-triazoline-3,5-dione, gave a 1:1 adduct (1), m.p. 160° (decomp.), $[\alpha]_{D}^{21} - 185^{\circ}$ (acetone). The n.m.r. signal at τ 9.5—9.0 (s, 1H, replaceable with D₂O) may be ascribed to NH absorption; this is confirmed by the i.r. spectrum, v_{max} 3450 and 3160 cm⁻¹. The 7α -orientation is consistent with the derivation of (1) by an α -face approach of the reagent which results in an 8(14)-as opposed to an 8(9)-double bond. The location of a double bond at 8(14) is also consistent with the downfield shift¹ of the C-18 methyl signal relative to the parent steroid (1), and with the n.m.r. spectra² of cognate 7α -8(14)-ene adducts.

When a solution of (1) in 'aged' chloroform (or in 0.001 methanolic HCl) was refluxed during 10 min, tetrahydro-4phenyltriazole-3,5-dione and 4,4-dimethylcholesta-5,7,14-(15)-trien-3-one (90%), m.p. 157°, were formed. The same products were produced almost immediately when a solution of (1) in benzene was treated with BF_3 -Et₂O. Reduction of 4,4-dimethylcholesta-5,7-14(15)-triene-3-one with LiAlH₄ gave 4,4-dimethylcholesta-5,7,14(15)-trien-3 β -ol (75%), m.p. 137-139°, clearly different from an authentic specimen of 4,4-dimethylcholesta-5,7,9(11)-trien-3 β -ol.³



Other derivatives of 3-oxo-4,4-dimethylcholesta- and 3-oxo-4,4-dimethylergosta-5,7-diene reacted similarly.

(2)

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Oxidation of the adduct (2; R = H, HO) with 4n-chromic acid gave the ketone (2; R = O), which at room temperature in benzene, containing BF3-Et2O rapidly formed cholesta-4,6,8(14)-trien-3-one, m.p. 61-63°. Ergosterol similarly gave ergosta-4,6,8(14),22-tetraen-3-one, m.p. 113-115°4 previously isolated as a fungal metabolite.⁵

All new compounds had the requisite spectral and analytical properties.

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