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DEAMINATION OF 19-NORABIETA-8,11,13-TRIEN-4-AMINE

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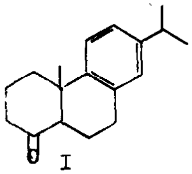
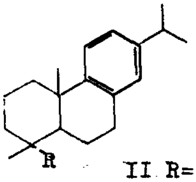
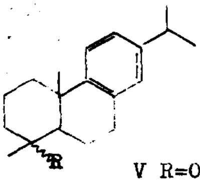
18,19-Dinorabieta-8,11,13-trien-4-one (I), a valuable intermediate in the conversion of the resin acid abieta-8,11,13-trien-19-oic acid (II) into compounds suitable for the synthesis of steroids, has been prepared in varying success.[3-8] The exocyclic alkene, 19-norabieta-4(18),8,11,13-tetraene (VII), is an important precursor to the formation of this ketone (I).


I

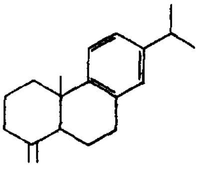

II R=COOH
III R=NCO
IV R=NH_2


V R=OH
VI R=OAc

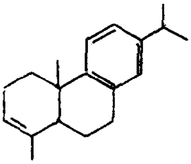
We wish to report an alternative high-yield route to I <u>via</u> the nitrous acid deamination of 19-norabieta-8,11,13-trien-4-amine (IV). Zeiss and Martin[5] have reported that treatment of the C-4 isocyanate (III) with mineral acid did not give satisfactory yields of the amine (IV). In this present work however, we have found that hydrolysis of a cold (0°) ethereal solution of III with 85% (w/w) sulphuric acid resulted in the formation of the tertiary amine (IV, 73%), picrate m.p. 218-220° (lit.,[7] 222-223°). $\nu_{max.}^{CCl_4}$ 3300, 1620 cm.$^{-1}$ (N-H). δ ($CDCl_3$) 1.12 (C_{18}-Me), 1.17 (C_{20}-Me), 1.23 (doublet, J=7 c/s, $(Me)_2CH$-), 1.75 (NH_2), 6.94-7.31 (aromatics). Reaction of IV with saturated sodium nitrite in 5% (v/v) acetic acid at 4° for 24 hr gave: 19-norabieta-8,11,13-trien-4ξ-ol (V, 10%), m.p. 91.5-92.5° (from light petroleum), $\nu_{max.}^{KBr}$ 3425, 1136 cm.$^{-1}$ (O-H), δ (CCl_4) 1.07 (C-H)(D_2O), 1.12 (C_{18}-Me), 1.17 (C_{20}-Me), 1.21 (doublet, J= 7c/s, $(Me)_2CH$-), 6.73-7.23 (aromatics); 19-norabieta-8,11,13-trien-4ξ-ol acetate (VI, 6%), $\nu_{max.}^{CS_2}$ 1745, 1250 cm.$^{-1}$ (acetate); and an alkene mixture (45%).

NMR analysis of the mixture of alkenes indicated the presence of: 65% of the $\Delta^{4(18)}$ isomer (VII), $\nu_{max.}^{CS_2}$ 3100, 890 cm.$^{-1}$ (=CH_2), δ (CCl_4) 0.99 (C_{20}

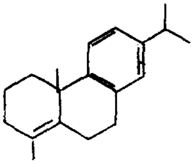
Me), 1.22 (doublet, J=7 c/s, $(Me)_2CH-$), 4.59, 4.84 ($=CH_2$), 6.80-7.30 (aromatics); 26% of the Δ^3 alkene (VIII), δ (CCl_4) 1.03 (C_{20}-Me), 1.22 (doublet, J=7 c/s, $(Me)_2CH-$), 1.34 (C_{18}-Me), 5.45 (C_3-H); and 9% of the Δ^4 isomer (IX).



VII



VIII



IX

Oxidation of the hydrocarbon mixture with OsO_4 gave I (75%). $\nu_{max.}^{CCl_4}$ 1718 cm.$^{-1}$ (C=O). δ (CCl_4) 1.02 (C_{20}-Me), 1.21 (doublet, J=7 c/s, $(Me)_2CH-$) 6.76-7.35 (aromatics).

The deamination products obtained from the equatorial amine (IV) show little resemblance to those resulting from the action of nitrous acid on the aminosteroids[9,10] aminodecalins[11] and the aminohydrindanes.[12,13]

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