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THE SYNTHESIS OF 32-OXYGENATED LANOSTANE DERIVATIVES

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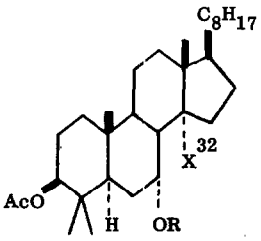
32-Oxygenated derivatives of lanostane have been postulated as intermediates in the biosynthesis of steroids from lanosterol[1]. We had completed a convenient synthesis of such compounds when we noted the recent communication[2] by Dr. Fried and his colleagues in which the same objective was enunciated. Subsequent correspondence with Dr. Fried revealed his continued interest in the problem which has culminated in the Communication which appears synchronously with the present manuscript. We thank Dr. Fried cordially for the courteous exchange of information which has made possible the simultaneous publication of both sets of results.

3β-Acetoxylanostan-7α-ol[3] (I, R = H, X = Me) was converted to its nitrite (I, R = NO, X = Me), m.p. 157 - 158°, $[\alpha]_D$ (all rotations in $CHCl_3$ at C = 1) - 74°, with pyridine-nitrosyl chloride. Photolysis[4] of this nitrite in dry benzene using a 125 w. high pressure mercury arc lamp gave the expected oxime (60%) (I, R = H, X = (CH = NOH)), m.p. 159° and 177 - 179°, $[\alpha]_D$ - 15°. On refluxing with acetic anhydride containing sodium acetate the diacetate-nitrile (I, R = Ac, X = CN), m.p. 233°, was obtained.

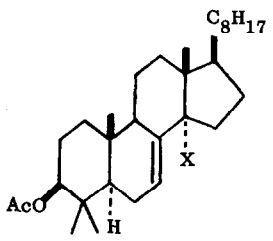
The oxime (I, R = H, X = (CH = NOH) in dry pyridine at room temperature, treated with methanesulphonyl chloride and left overnight at 0 - 5°, gave the expected mesylate-nitrile (85%) (I, R = CH_3SO_2, X = CN). This was refluxed in

collidine under nitrogen for 21 hr. to furnish the unsaturated nitrile (75%) (II, X = CN), m.p. 139 - 140°, $[\alpha]_D$ + 30°. This unsaturated nitrile in dry tetrahydrofuran was shaken with lithium aluminium hydride at room temperature for 3 days. Pouring into water, reacetylation with pyridine-acetic anhydride and crystallisation from methanol gave the desired aldehyde (40%) (II, X = CHO) as needles, m.p. 144 - 145°, $[\alpha]_D$ + 24°.

All compounds had the expected spectroscopic and analytical data.



(I)



(II)

REFERENCES

1. F. Gautschi and K. Bloch, J. Amer. Chem. Soc., 79, 684 (1957); J. Biol. Chem., 233, 1343 (1958).
2. J. Fried, J. W. Brown and M. Applebaum, Tetrahedron Letters, 849 (1965).
3. D.H.R. Barton and B.R. Thomas, J. Chem. Soc., 1842 (1953).
4. D.H.R. Barton, J.M. Beaton, L.E. Geller and M.M. Pechet, J. Amer. Chem. Soc., 83, 4076 (1961).