Molbank **2009**, M616

OPEN ACCESS

molbank

ISSN 1422-8599

www.mdpi.com/journal/molbank

Short Note

Mercuric(II) Acetate Oxidation of Steroidal Exocyclic α,β-Unsaturated Ketone: Transformation into a Cyclic Ether

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Received: 22 June 2009 / Accepted: 3 August 2009 / Published: 1 September 2009

Abstract: 16-Dehydropregnenolone acetate (16-DPA) (**1**), an exocyclic α,β-conjugated ketone having a steroidal skeleton, when treated with mercuric(II) acetate in acetic acid furnished a single compound identified as (**2**). The structure of compound (**2**) has been elucidated on the basis of spectral data analysis (IR, NMR and MS).

Keywords: 16-DPA; mercuric(II) acetate; exocyclic α,β-conjugated ketone; steroidal skeleton

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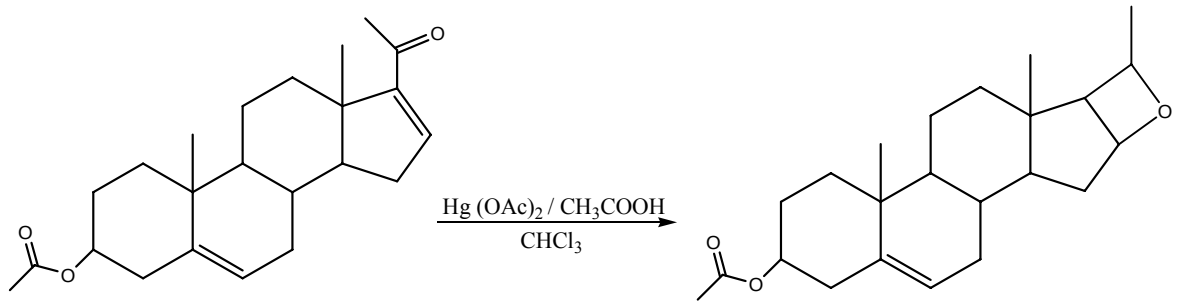
In the course of our continuous study on the transformative reactions of steroids and triterpenoids [1–5], we report herein the transformation of 16-DPA into a cyclic ether formed on ring-D on the steroidal skeleton.

Oxidative transformation of steroids and triterpenoids using mercuric(II) acetate has been reported earlier by a number of research groups. Depending on the nature of the substrate, this oxidation has been reported to furnish lactones [6], cyclic ethers [6–8] and some other products [9–12] from steroids and triterpenoids. People have reported the formation of $\Delta^{7,9}$-allo-steroids from Δ^{7}-allo-steroids [13], conversion of substituted double bond of steroidal systems into α,β-unsaturated ketones [14], mercuration and associated rearrangement of α,β-unsaturated steroidal ketones [15] by using the same reagent.

Encouraged by these findings, we undertook the present investigation towards the oxidative trans-formation of an exocyclic α,β-unsaturated ketone, taking 16-DPA as a representative steroidal skeleton. The transformation introduces a cyclic ether onto the ring-D of 16-DPA, involving the

carbonyl oxygen and the double bond in its α,β-position. A single-step conversion of exocyclic α,β-conjugated ketone functionality of a steroid into a four-membered cyclic ether which may possess potent biocidal activity [16], preserves the main significance of the study. The result of this investigation is reported in this communication.



1 2

Experimental

16-DPA (0.5 g) was dissolved in chloroform (12.5 mL) and a solution of mercuric(II) acetate (9 g) in hot glacial acetic acid (70 mL) was added. The reaction mixture was maintained at 100 ºC in an oil bath for 4 hours. On cooling, the precipitated mercuric(I) acetate was filtered off and the whole filtrate was diluted with water and extracted with chloroform. The chloroform layer was washed well with water and then dried over anhydrous sodium sulphate. Removal of chloroform gave an orange solid which was dissolved in pyridine and H_2S was passed for 2 hours. The black reaction mixture was filtered and pyridine was removed by very dilute HCl and then extracted with ether. The brownish black residue (0.38 g) so obtained was then chromatographed over silica gel. The product was obtained using ethyl acetate and petroleum ether mixture (1:6) as eluent and it was recrystallised from absolute alcohol to get white crystals of m.p. 132-134 ºC, Yield: 0.25 g.

IR (KBr, cm^{-1}): υ 1726, 1696, 1240, 1030 and 668.

^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.37 (s, 1H, CH), 4.61 (s, 1H, CH), 3.85-4.20 (m, 2H, CH), 2.95 (dd, *J* = 3.0 Hz and 6.0 Hz,1H, CH), 2.18 (d, *J* = 6.0 Hz, 3H, CH_3), 2.03 (s, 3H, CH_3), 1.02 (s, 3H, CH_3), 0.66 (s, 3H, CH_3).

^{13}C-NMR (300 MHz, $CDCl_3$): δ 170.5 (>CO), 139.6 (=C_5), 121.9 (=C_6H), 73.7 (-O-CH), 71.1 (-O-CH), 70.6 (-C_3H), 55.6, 49.6, 47.0, 45.6, 38.5, 37.9, 36.8, 36.5, 33.3, 31.8, 31.5, 31.3, 27.6, 21.4, 20.8, 19.2, 14.2.

MS: m/z = 358 (M^+), 343, 315, 298, 297 (100%).

Elemental Analysis: Calculated for $C_{23}H_{34}O_3$ (358.52): C, 77.05%; H, 9.56%; O, 13.39%. Found: C, 77.08%; H, 9.61%; O, 13.45%.

Acknowledgement

The authors thank to CDRI, Lucknow, India, for the mass spectral data and elemental analysis.

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