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E- HOMO REARRANGEMENT OF THE NOR- KETO LACTONE DERIVED FROM THE Hg(ic) ACETATE OXIDATION PRODUCT OF ACETYL BETULINIC ACID.

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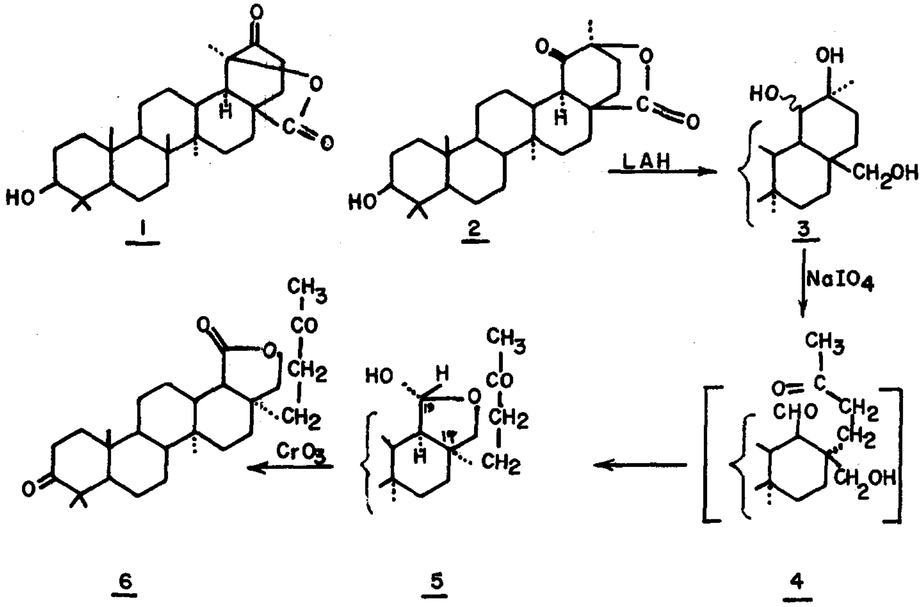
The nor-ketolactone[1] obtained by ozonolysis of the product derived from the mercuric acetate oxidation of acetyl betulinic acid was found to undergo rearrangement[2,3] on treatment with K-tert. butoxide in t-butyl alcohol. Recently Vystrcil and Blecha[4] advanced structure 2 for the rearranged product mainly from physical and mechanistic grounds. To decide between the alternative structures 1 and 2, we undertook chemical degradative studies which gave further support to structure 2 for the rearranged lactone. The lactone 2 on LAH reduction gave the tetrol 3 as a mixture of epimers, $C_{29}H_{50}O_4$, m.p. 274-5°, ν_{max}^{Nujol} 3340 cm^{-1} (OH). Cleavage of the tetrol 3 with sodium metaperiodate gave, instead of the expected aldehyde 4, a product m.p. 217-8°, $C_{29}H_{48}O_4$ to which we assign structure 5 on the basis of the following evidences: ν_{max}^{Nujol} 1680 (H-bonded carbonyl), 3460 (OH, H-bonded) and 3560 cm^{-1} (free OH), $\lambda_{max}^{Ethanol}$ 270 mμ (ϵ, 60), NMR (220 Mc) peaks at δ 5.15 (C-19H, singlet), δ 3.75 (-CH$_2$-O-, C-28, quartet), δ 3.5 (OH, absent after D$_2$O exchange), δ 3.25 (C-3H, quartet), δ 2.45 (CH$_3$COCH$_2$-C, sextet), δ 2.17 (3H, -COCH$_3$, singlet) and methyl peaks at δ 0.95, δ 0.90, δ 0.80 and δ 0.75 (5 methyl groups). Absence of the aldehyde proton signal in the NMR indicates that a hemiacetal has been formed with the C-28 hydroxyl group. A shift in the I.R. carbonyl band (1680 cm^{-1}) coupled with the appearance of a different hydroxyl absorption band (3460 cm^{-1}) suggests that both the lactol hydroxyl at C-19 and the newly generated carbonyl group in the C-17 side chain are involved in hydrogen bonding.

Construction of a Drieding model of the lactol 5 shows that the lactol bridge should be on the β-face of the molecule and also that the configuration of C-19 OH should be quasi-axial. In this conformation of the molecule 5 the dihedral angle between C-18H and C-19H is nearly 90°, making the interaction between them very nearly zero, which accounts for the singlet at δ 5.15 for the C-19H. Further, the model shows that the C-19 OH group can come very close to -CO- group in the side chain at C-17 and participate in hydrogen bonding.

Structure 5 is further supported by its oxidation to a γ-lactone 6, m.p. 213-4° $C_{29}H_{44}O_4$, ν_{max}^{Nujol} 1710(C_3-carbonyl), 1768 cm^{-1}(γ-lactone).



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