Tetrahedron Letters No.32, pp. 3589-3590, 1968. Pergamon Press. Printed in Great Britain.

LITHIUM ALUMINIUM HYDRIDE REDUCTION OF A CYCLIC ANHYDRIDE TO A δ-LACTONE

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(Received in UK 29 April 1968; accepted for publication 13 May 1968)

The controlled $LiAlH_4$ reduction of several 5-membered ring anhydrides has been shown[1,2,3,4] to give γ-lactones. A recent report[5] that only the more hindered carbonyl group of the anhydride is reduced, prompts us to record results obtained during another investigation. Reduction of the 6-membered ring anhydride (I)[6], derived from gibberellin A_{13}, with excess of $LiAlH_4$ in tetrahydrofuran at -55° for 1 hour gave a δ-lactone in 50% yield, ν_{max} 3490 (OH), 1733 (δ-lactone), and 1700 (C=O of CO_2H) cm^{-1}. Its NMR spectrum* contained an AB quartet centred at 5.59 and 5.97τ (J = 12.5 cps) assigned to the $\equiv C\cdot CH_2\cdot O\cdot CO\cdot$ group and a 3-proton singlet at 9.04τ due to the 1β-methyl group. Comparison of the chemical shift of the latter with those of the 1β-methyl groups in gibberellin A_{15} methyl ester (III)[7] and the gibberellin A_{23} derivative (IV)[8], which are found at 8.85 and 8.81τ respectively, shows that the δ-lactone contains the grouping $\cdot CO\cdot O\cdot CH_2\cdot \overset{|}{C}\cdot Me$ rather than $\cdot O\cdot CO\cdot \overset{|}{C}\cdot Me$. Hence the δ-lactone has structure (V). Inspection of a Dreiding model of (I) shows that the 1α-carbonyl is more hindered than the 4aα-group and this is confirmed by the reaction of (II) with methanol at 120° which gives only one ester. The latter has been shown to have structure (VII) because on oxidation with Jones reagent it gave the keto-ester (VIII) and no carbon dioxide was evolved. Thus, in contrast to the results of Bloomfield and Lee[5], the less hindered carbonyl group of (I) was reduced by $LiAlH_4$. This is in agreement with the observation [1] that $LiAlH_4$ reduction of naphthalene-1,2-

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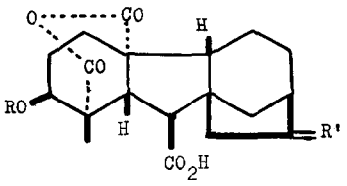
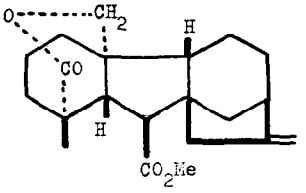
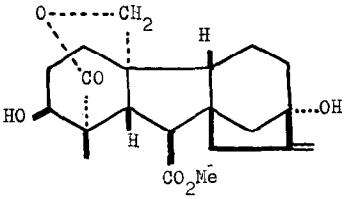
* NMR spectra were determined on a Varian A60 instrument in $CDCl_3$ solution.



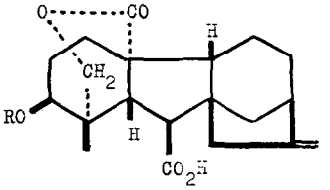
I R = Ac, R' = CH_2
II R = H, R' = O



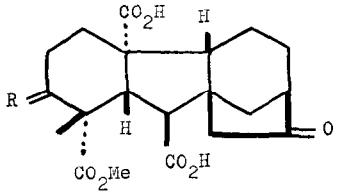
III



IV



V R = H
VI R = Ac



VII R = H, OH
VIII R = O

dicarboxylic acid anhydride gave the lactone of 2-hydroxymethylnaphthalene-1-carboxylic acid.

A minor product from the $LiAlH_4$ reduction of (I) was the δ-lactone (VI), τ_{max} 9.14 (3H, singlet; 1β-methyl), 7.88 (3H, singlet; acetyl), 7.36 (2H, singlet; 10- and 10a- protons), 5.92 and 5.58 (J = 13 cps) (>C·CH_2·O·), and 5.04 (3H, broad; = CH_2 and >CHOAc).

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