

Sodium Borohydride Reduction of Glycidic Esters and Lactones

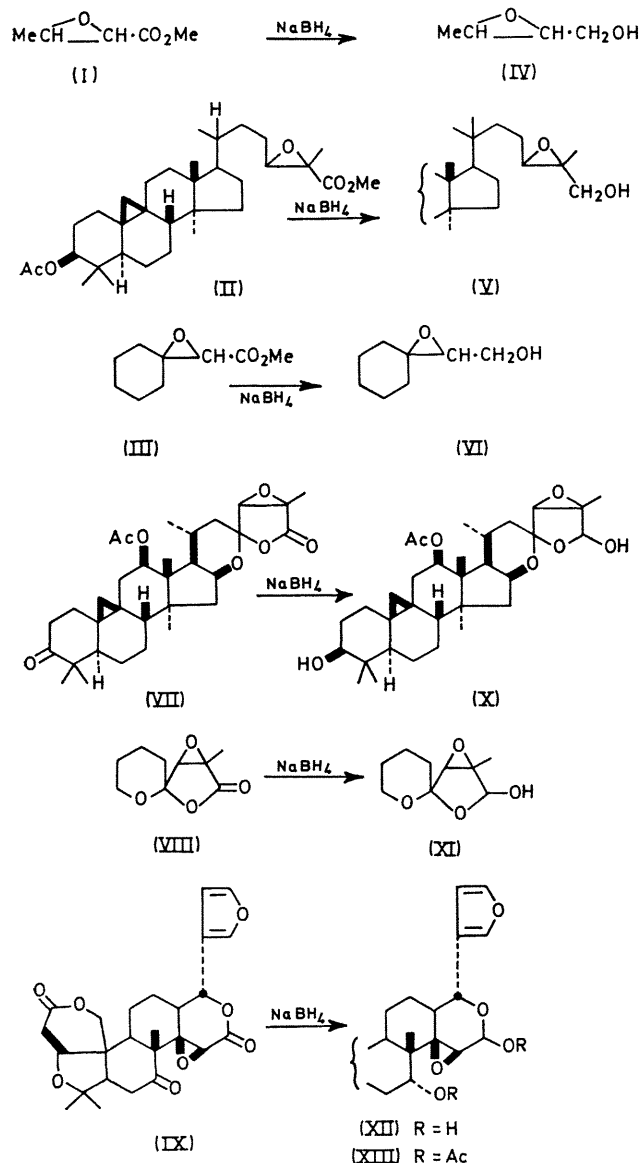
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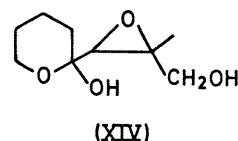
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Summary Whereas glycidic esters are reduced by sodium borohydride to hydroxymethyloxirans, glycidic lactones are selectively reduced to the corresponding lactols



ESTERS and lactones are reduced very slowly by sodium borohydride to give alcohols and diols¹. The reduction rate is increased by using magnesium or lithium borohydride instead of NaBH_4 ². Furthermore, nucleophilic attack by the hydride is facilitated by electron-withdrawing groups α to the ester group³. We report the results of the reduction with NaBH_4 of epoxy-esters (I), (II), and (III) and epoxy-lactones (VII), (VIII), and (IX).[†] Epoxy-esters (I), (II), and (III) are quickly reduced by NaBH_4 to epoxy-alcohols (IV), (V), and (VI), in very high yields (85–90%) [0.5 mmoles of epoxy-ester (I) in a 15% dioxan solution was added at room temperature to a 1:1 dioxan–water solution containing 0.7 mmoles of NaBH_4 . The reduction was complete in 30 min]. Thus glycidols ($\alpha\beta$ -epoxy-alcohols) can be prepared easily by reduction of the corresponding esters with NaBH_4 . The keto-epoxy-lactone (VII), derived from the acetyl-acetol (X), a triterpenoid genin,⁴ under experimental conditions described above, affords (X) by reduction with NaBH_4 in a very short time (80% yield). The keto-group is reduced to hydroxyl, but the lactone function is reduced only to the hemiacetal stage, and the acetate group is not cleaved. The same behaviour towards NaBH_4 is shown by the synthetic glycidic lactone (VIII), which yields the lactol (XI) (40%). Limonin (IX), the bitter principle of lemon seeds,⁵ has been reduced to limonidol (XII) (90%), which on acetylation affords the diacetate (XIII).[‡] Even in this case the keto-function and the epoxy-lactone are reduced, while the δ -lactone remains unaffected. Lactols (X) and (XI) are slowly reduced further on prolonged reaction with NaBH_4 , but we did not succeed in isolating products like diol (XIV), probably on



account of their high reactivity. Hence, glycidic lactones can be reduced selectively to the hemiacetal stage, like other lactones carrying electron-withdrawing groups in the neighbourhood of a carbonyl function, such as lactones of aldonic acids.⁷

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[†] Satisfactory analyses and spectra (ν , n , m , r) have been obtained for all new compounds. Physical data will be reported in the full paper.

[‡] Under different experimental conditions, the NaBH_4 reduction is limited to the keto-group of limonin (IX).⁶

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