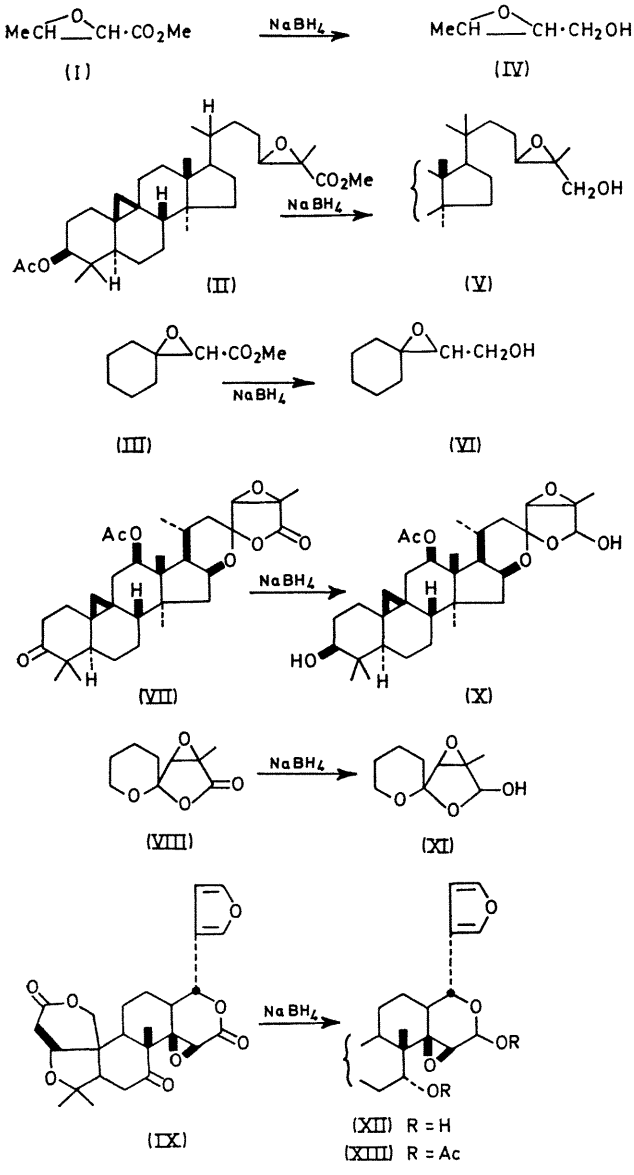
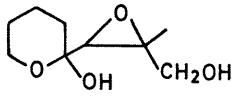
Sodium Borohydride Reduction of Glycidic Esters and Lactones

By STEFANO CORSANO
(*Istituto di Chimica delle Sostanze Organiche Naturali, Università di Perugia*, 06100 *Perugia, Italy*)
and GIOVANNI PIANCATELLI*
(*Istituto di Chimica Organica-I Cattedra, Università di Roma* 00100 *Roma, Italy*)

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 diols [1] 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 group [3] 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 limondiol (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



(XIV)

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]

We thank the Italian C N R for financial support

(*Received, May 6th*, 1971, *Com* 715)

† Satisfactory analyses and spectra (i r , 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]

[1] H O. House, "Modern Synthetic Reactions", Benjamin, New York, 1965, p 32
[2] H C Brown, E J Mead, and B C Subba Rao, *J Amer Chem. Soc* , 1955, **77**, 6209
[3] (a) E Schenker, *Angew Chem* , 1961, **73**, 81, (b) E Schenker, "Newer Methods of Preparative Organic Chemistry", vol. IV, Verlag Chemie, Weinheim, 1968, p 196
[4] S Corsano, G Piancatelli, and L Panizzi, *Gazzetta*, 1969, **99**, 915
[5] D H R Barton, S K Pradhan, S Sternhell, and J F Templeton, *J Chem Soc* , 1961, 255
[6] A Melera, K Schaffner, D Arigoni, and O Jeger, *Helv Chim Acta*, 1957, **40**, 1420
[7] (a) M L Wolfrom and K Anno, *J. Amer Chem Soc* , 1952, **74**, 5583, (b) T Hori, A K Kiang, K Nakanishi, S Sasari, and M C. Woods, *Tetrahedron*, 1967, **23**, 2649, (c) J Polonsky and N Bourguignon-Zylber, *Bull Soc chim France*, 1965, 2793, (d) T. Murata, S Imai, and M Imanishi, *Tetrahedron Letters*, 1965, 3215