Asymmetric Birch Reduction of Furoic Acids

By TAKAMASA KINOSHITA and TOSHIO MIWA*
(*Faculty of Science, Osaka City University, Osaka* 558, *Japan*)

Summary The Birch reduction of furoic acids in the presence of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose gave optically active dihydrofuroic acids.

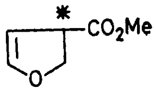
INCH'S group[1] and other workers[2] have reported asymmetric reactions with Grignard reagents or with lithium aluminium hydride complexes of some sugar derivatives.

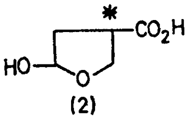
The Birch reduction of 2- or 3-furoic acid gave 2,5-[3] or 2,3-dihydrofuroic acid,[4] respectively. The use of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (G) as the proton source in the Birch reduction caused asymmetric reduction.

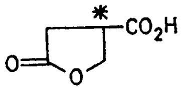
The reduction of 3-furoic acid with sodium and (G) in liquid ammonia gave an optically active acid, which after esterification with diazomethane, was isolated as an optically active methyl 2,3-dihydro-3-furoate (**1**), colourless liquid, b.p. 83—84°/30 mm; $[\alpha]_D$ −8·7°; M^+ m/e 128; ν_{max} 3120, 1735, 1620 cm^{-1}.

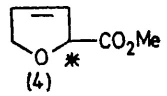
The acid [assumed to be 5-hydroxytetrahydro-3-furoic acid, (**2**)] obtained by leaving the acidified reduction mixture to stand overnight, was oxidized with silver oxide, to give paraconic acid (**3**), b.p. 150—160° (bath)/0·05 mm, of optical activity, $[\alpha]_D$ +1·9° (MeOH). Paraconic acid with *R* configuration has an optical activity, $[\alpha]_D$−60·4°,[5] thus the asymmetric reduction occurred with an approximate optical yield of 3%.

The reduction of 2-furoic acid in similar manner gave an optically active methyl 2,5-dihydro-2-furoate (**4**), b.p. 94°/35 mm; $[\alpha]_D$ +3·5°. The absolute configuration of the compound (**4**) is under investigation.


(1)


(2)


(3)


(4)

These asymmetric reductions are attributable to protonation by a chiral source and this type of asymmetric reaction has probably no precedents.

(*Received*, 7*th November* 1973; *Com.* 1538.)

[1] T. D. Inch, G. J. Lewis, G. L. Sainsbury, and D. J. Sellers, *Tetrahedron Letters*, 1969, 3657.
[2] O. Cervinca and A. Fabryova, *Tetrahedron Letters*, 1967, 1179.
[3] L. Rosenblum, Ph.D. Thesis, Ohio State University, 1952.
[4] T. Kinoshita, K. Miyano, and T. Miwa, *Bull. Chem. Soc. Japan*, submitted for publication
[5] S. Ito, Y. Fujise, and A. Mori, *Chem. Comm.*, 1965, 595.