Partial Reduction of Unsubstituted Aldonolactones with Lithium Aluminium Hydride

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THE partial reduction of aldonolactones to the corresponding aldoses is a reaction frequently used in sugar chemistry.[1] Although several complex hydrides have been employed,[2] little attention has been paid to the use of lithium aluminium hydride; the reagent has been used mainly for the reduction of lactones to alditols.[3] Unsubstituted aldono-lactones are not very soluble in the solvent (ether or tetrahydrofuran) usually employed with lithium aluminium hydride, a factor which has probably prevented application of the reagent for the partial reduction of aldonolactones. The partial reduction, with lithium aluminium hydride, of aliphatic or aromatic lactones or esters to the corresponding aldehydes or hydroxy-aldehydes has been described.[4]

We have described[5] the partial reduction of 4,6-dideoxy-L-*ribo*-hexono-1,5-lactone to 4,6-dideoxy-L-*ribo*-hexopyranose by means of aqueous ammonia–borane (NH_3BH_3) or sodium borohydride and by sodium aluminium hydride or lithium aluminium hydride in tetrahydrofuran. The last-named reagent gave the best yield.

We now report the use of lithium aluminium hydride for the partial reduction of aldonolactones. A 1 : 1 mixture of pyridine and tetrahydrofuran was a suitable solvent with a lactone concentration of *ca.* 0·1M. To this solution was added, under an atmosphere of nitrogen at *ca.* $-70°$, a 100% excess (with allowance for the active hydrogen atoms of the hydroxy-groups) of a clear solution (1·5M) of lithium aluminium hydride in tetrahydrofuran. After 30 min. the temperature was allowed to rise to 0° during a further 30 min. The course of the reduction could be conveniently followed by t.l.c.[6]

The following aldonolactones were reduced by the above procedure to give (yields determined by reductimetric titration[7]) D-arabino-1,4-lactone (59%), D-galactono-1,4-lactone (65%), L-mannono-1,4-lactone (73%), D-glucono-1,4-lactone (65%), D-*glycero*-L-*manno*-heptono-1,4-lactone (70%), and L-rhamnono-1,4-lactone (74%). Apart from small amounts (1—3%) of unchanged lactone the remaining material was the corresponding polyhydric alcohol.

In the case of D-galactono-1,4-lactone 91% of a mixture of the D-galactose and galactitol was isolated after destruction of the excess of reductant with aqueous methanol, removal of cations with Dowex 50 W (H^+ form), and unchanged lactone with Dowex 2 (OH^- form). The mixture contained[7] 65% of D-galactose. (The deionisation[8] of the reduction product was carried out as follows. The aqueous solution (50 ml.) of the product, obtained by reduction of D-galactono-1,4-lactone, (356 mg.) was shaken (15 min.) with Dowex 50W × 8 100/200 mesh (H^+ form) (30 ml.), the resin was filtered off and washed with water (80 ml.). The combined filtrates were concentrated to 50 ml. and shaken (15 min.) with Dowex 2 × 8 100/200 mesh (OH^- form) (3 ml.). The resin was filtered off and washed five times with 5 ml. of water.

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[1] R. L. Whistler and M. L. Wolfrom, "Methods in Carbohydrate Chemistry", Academic Press, New York, 1963, vol. II, p. 63. J. Staněk, M. Černý, J. Kocourek, and J. Pacák, "The monosaccharides", Czechoslovak Academy of Sciences, Prague, 1963, p. 144.

[2] M. L. Wolfrom and H. B. Wood, *J. Amer. Chem. Soc.*, 1951, **73**, 2933; P. Kohn, R. H. Samaritano and L. M. Lerner, *J. Amer. Chem. Soc.*, 1965, **87**, 5475; T. A. Giudici and A. L. Fluharty, *J. Org. Chem.*, 1967, **32**, 2043.

[3] R. K. Ness, H. G. Fletcher, jun., and C. S. Hudson, *J. Amer. Chem. Soc.*, 1951, **73**, 4759; R. E. Reeves, *J. Amer. Chem. Soc.*, 1954, **76**, 934.

[4] G. E. Arth, *J. Amer. Chem. Soc.*, 1953, **75**, 2413; F. Korte, U. Claussen, and K. Göhring, *Tetrahedron*, 1962, **18**, 1257; L. I. Zakharkin, V. V. Gavrilenko, N. D. Maslin, and I. M. Khorlina, *Tetrahedron Letters*, 1963, 2087.

[5] J. Němec and J. Jarý, *Coll. Czech. Chem. Comm.*, in the press.

[6] J. Němec, K. Kefurt, and J. Jarý, *J. Chromatog.*, 1967, **26**, 116.

[7] M. Jureček, *Organická analysa*, Czechoslovak Academy of Sciences, Prague 1957, vol. II, p. 306.

[8] P. W. Austin, F. E. Hardy, J. G. Buchanan, and J. Baddiley, *J. Chem. Soc.*, 1963, 5350.