Novel Aromatization of Inositols in Dimethyl Sulphoxide–Acetic Anhydride

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DIMETHYL SULPHOXIDE in acetic anhydride has proved to be an efficient reagent for the oxidation of an isolated or sterically hindered secondary alcoholic group to a ketone group in steroids[1] and partly substituted carbohydrates.[2]

A unique, one-step aromatization of inositols (cyclohexanehexaols) following treatment with dimethyl sulphoxide–acetic anhydride is now reported.

myo-Inositol (2 g.) was stirred with a mixture of dry dimethyl sulphoxide (30 ml.), acetic anhydride (10 ml.), and dry pyridine (5 ml.) at 60—65° for 45 min. Treatment of the red-brown reaction mixture with ice-water deposited 1·9—2·1 g. (54–60%) of penta-acetoxybenzene, m.p. 153—158°. Recrystallization from 4 : 1 (v/v) ethanol—acetic acid raised the melting point to 166—168°. The product was identical (infrared spectrum, mixture m.p., and chromatography) with an authentic sample.[3]

Penta-acetoxybenzene has also been obtained in good yield from *epi*-inositol, *dextro*-inositol, *lævo*-inositol, *muco*-inositol, and *scyllo*-inositol. Apparently, dimethyl sulphoxide–acetic anhydride is not a stereospecific oxidizing agent, in contrast to catalytic[4] or bacterial[4] oxidants, as *scyllo*-inositol, which has no axial hydroxyl groups and is known to be inert either to catalytic or bacterial oxidation,[4] is converted into penta-acetoxybenzene as readily as are the other inositols.

Surprisingly, penta-acetoxybenzene was not formed from either *myo*-inos-2-ose or DL-*epi*-inos-2-ose, the known oxidation products obtained from *myo*-inositol.[5] However, penta-acetoxybenzene was produced when the starting material was "DL-*xylo*-4,5,6-trihydroxycyclohexenediolic acid", the enolic form of a diketoinositol that is obtained by oxidation of *myo*-inositol with nitric acid.[3b] Thus, the conversion of inositols into penta-acetoxybenzene probably proceeds through a form of the diketoinositol as an intermediate.

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