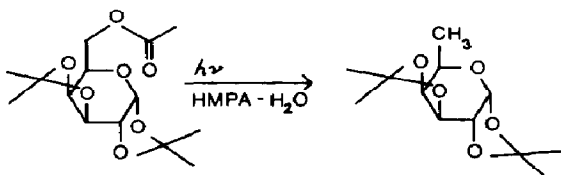


Organic Photochemical Synthesis

6-Deoxy-1,2:3,4-di-*O*-isopropylidene- α -D-galactopyranose



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1. Procedure

The apparatus consists of 12 low pressure mercury lamps (TUV 15 Philips) (note 1) arranged in a circular bank of diameter 45 cm. The reaction vessels are five quartz tubes 30 cm long and 1 cm in internal diameter supported on a merry-go-round of diameter 20 cm with its axis at the centre of the circular bank. The apparatus is air cooled.

A solution of 6-*O*-acetyl-1,2:3,4-di-*O*-isopropylidene- α -D-galactopyranose (note 2) (3 g, 0.01 mol) in 100 cm³ of a mixture of hexamethylphosphoramide (HMPA): H₂O (95:5) (note 3) in the five quartz tubes is irradiated for 7 h (notes 4 and 5). All the starting material is consumed as shown by thin layer chromatography (TLC) monitoring (note 6).

The irradiated solution is then poured into cold water (0 °C, 500 cm³) and extracted with ether (4 × 50 cm³). The combined ethereal extracts are washed with water (3 × 25 cm³) and dried over sodium sulphate. After filtration the ether is removed under reduced pressure to give 2.1 g (85%) of the desired 6-deoxy-1,2:3,4-di-*O*-isopropylidene- α -D-galactopyranose; the nuclear magnetic resonance (NMR) spectra [1] and $[\alpha]_D$ [1, 2] correspond to those of the pure material (note 7).

2. Notes

(1) The checkers used a single quartz tube, and the source of 254 nm radiation was a set of RUL-2537 low pressure lamps in a Rayonet RPR-208 photochemical reactor (Southern New England Ultraviolet Company).

(2) The starting material was prepared according to ref. 3.

(3) Technical grade HMPA, generously supplied by Compagnie Française de l'azote, was distilled under reduced pressure (boiling point, about 80 °C at 0.3 mmHg).

(4) The light is absorbed by HMPA [4, 5] ($\epsilon_{254} = 0.3$). The use of co-solvents or higher concentrations of acetate may slow down the rate of the photoreduction.

(5) The solution does not need to be degassed. During the photolysis some hydrogen gas is evolved [5], so the tubes must be vented.

(6) A few drops of the solution are treated with an excess of water and ether (0.5 cm³) and the ethereal layer is examined using silica gel TLC (eluent, C₆H₁₂:CH₃CO₂C₂H₅ (6:4)). The irradiation is stopped when all the starting material has disappeared. The checkers found that TLC did not give a clear indication of the conversion and used NMR analysis of a small extracted sample instead.

(7) The purity of the deoxysugar is monitored by NMR and by gas-liquid chromatography analysis (6 ft × 1/8 in; 10% SE 30 on 80-100 Chromosorb WAW HMDS; temperature, from 190 to 210 °C at 5 °C min⁻¹ and then 210 °C). Traces of HMPA may still be present, and filtration on silica gel is then necessary [1]. The checkers found that the NMR spectrum differed in one respect from the published information, in that the signal for one of the isopropylidene groups appeared as two singlets rather than as just one singlet.

3. Merits of the preparation

The deoxysugar is the only product formed in the photolysis from a readily available starting material. This photoreduction reaction of acetates is general and can be extended successfully to prepare deoxysugars at any of the 2, 3, 4, 5 or 6 positions [2] or to the preparation of dideoxysugars and trideoxysugars [6].

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