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SYNTHESIS OF 8-(D-GLUCO-PENTA-O-HYDROXYLPENTYL)-7-OXABICYCLO[4.2.0]OCTANE

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SYNTHESIS OF 8-(D-GLUCO-PENTA-O-HYDROXYLPENTYL)-7-
OXABICYCLO[4.2.0]OCTANE[†]

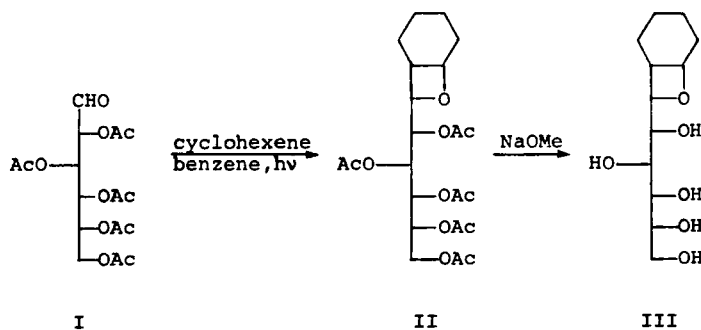
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Although the photoaddition of carbonyl compounds to olefins leading to oxetane rings has been intensively investigated,¹ the photoaddition of sugar aldehyde to olefin has rarely been studied. We have examined the photoaddition of cyclohexene to aldehydo-D-glucose pentaacetate (I) and obtained good yields of 8-(D-gluco-penta-O-acetylpentyl)-7-oxabicyclo[4.2.0]octane (II), purified by column chromatography of the product



mixture. Compound II was isolated as a syrup (65%) on thin layer chromatography. The faster moving oxetane II predominated by 4:1 and no attempts were made to purify the other slower moving minor products (four components by tlc). The oxetane formation likely results by way of a stable biradical in-

intermediate.² The syrupy oxetane II was deacetylated with sodium methoxide to yield crystalline 8-(D-gluco-penta-O-hydroxypentyl)-7-oxabicyclo[4.2.0]octane (III). The bicyclic oxetane structure was readily characterized³ by an intense infrared absorption band in the region of 930 cm^{-1} and the characteristic nmr signal of H-8 in the oxetane ring⁴ gave a doublet of doublet⁵ at δ 5.48 with $J_{1,8}$ 6 Hz. Both oxetanes II and III gave correct elemental analyses.

EXPERIMENTAL

Cyclohexene was purified prior to use by passing it through neutral alumina. Infrared spectra were obtained on a Perkin Elmer 727B spectrophotometer and NMR spectra were recorded on a Varian T-60 spectrophotometer.

8-(D-Gluco-penta-O-acetylpentyl)-7-oxabicyclo[4.2.0]octane

(II).- A solution of 30 g (0.077 mole) of I in 1100 ml of benzene and 500 ml of cyclohexene was irradiated for 5 hrs at $10-15^{\circ}$, using a 450 W Hanovia 679A-36 mercury arc lamp in a quartz immersion well without filter under oxygen-free nitrogen. The mixture was filtered to remove some insoluble polymeric materials and concentrated to a syrup. The syrup was chromatographed on a silica gel (J. T. Baker Chem. Co., 60-200 mesh) and eluted twice with benzene-ether (1:2, v/v) to yield 23.5 g (65%) of the fast moving, syrupy 8-(D-gluco-penta-O-acetylpentyl)-7-oxabicyclo[4.2.0]octane (II), R_f 0.73 in a solvent of ether-benzene (3:1, v/v). IR (neat): 1735 cm^{-1} (OAc) and 930 cm^{-1} (asymmetric ring stretching vibration involving the C-O bond in the oxetane ring³).

Anal. Calcd. for $C_{22}H_{32}O_{11}$: C, 55.92; H, 6.83.

Found: C, 55.84; H, 6.97.

8-(D-Gluco-O-hydroxylpentyl)-7-oxabicyclo[4.2.0]octane (III).-

To a cooled solution of 5 g (0.011 mole) of II in 35 ml of MeOH was added 55 ml of a freshly prepared 0.1 N NaOMe and the solution was kept at 0° for 4 hrs. The progress of the reaction was checked by TLC using CHCl₃-MeOH (3:1, v/v). When the deacetylation was complete, the solution was neutralized with IR-120 (H⁺) resin and filtered. The filtrate was concentrated to a syrup which was crystallized from MeOH-EtOAc to provide 2.5 g (93%) of 8-(D-gluco-penta-O-hydroxylpentyl)-7-oxabicyclo[4.2.0]octane (III), mp. 135-136°. IR (KBr): 3435 (H-bonded OH) and 948 cm⁻¹; NMR(pyridine-d₅): δ 5.48 (dd, 1H), 4.75 (m, 1H), 3.47-4.07 (m, 6H), 2.94 (t, 1H), 1.0-2.2 (m, 8H).

Anal. Calcd. for C₁₂H₂₂O₆: C, 54.94; H, 8.45.

Found: C, 54.97; H, 8.43.

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