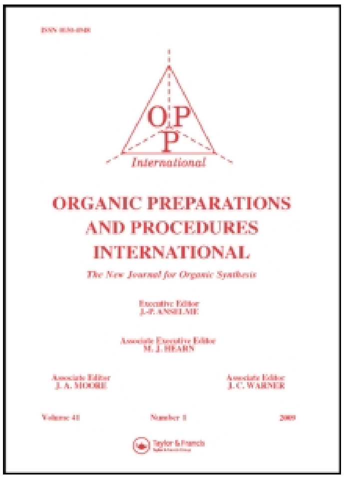

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SYNTHESIS OF 8-(D-GLUCO-PENTA-O-HYDROXYLPENTYL)-7-OXABICYCLO[4.2.0]OCTANE

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

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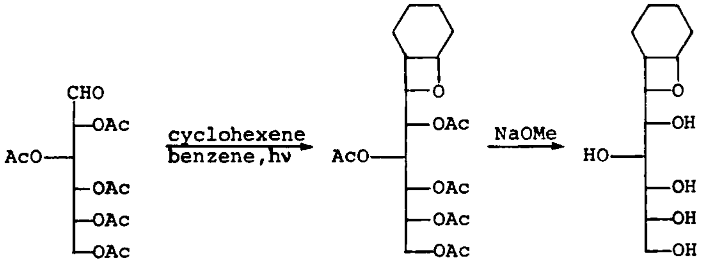
Although the photoaddition of carbonyl compounds to olefins leading to oxetane rings has been intensively investigated,[1] the photoaddition of sugar aldehyde to olefin has rarely been studied. We have examined the photoaddition of cyclohexene to aldehydo-D-glucose pentaacetate (I) and obtained good 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-



I II III

termediate.[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 characterized[3] by an intense infrared absorption band in the region of 930 cm^{-1} and the characteristic nmr signal of H-8 in the oxetane ring[4] gave a doublet of doublet[5] 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.

<u>8-(D-Gluco-penta-O-acetylpentyl)-7-oxabicyclo[4.2.0]octane</u> (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°, 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 ring[3]).

<u>Anal</u>. 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 $CHCl_3$-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-d_5): δ 5.48 (dd, 1H), 4.75 (m, 1H), 3.47-4.07 (m, 6H), 294 (t, 1H), 1.0-2.2 (m, 8H).

Anal. Calcd. for $C_{12}H_{22}O_6$: C, 54.94; H, 8.45.
Found: C, 54.97; H, 8.43.

REFERENCES

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1. A. Schoenber and A. Mustafa, Chem. Rev., 40, 191 (1947); G. S. Hammond, W. P. Baker and W. M. Moore, J. Am. Chem. Soc., 2795 (1961); G. Ported and P. Suppon, Proc. Chem. Soc., 191 (1964); P. De Mayo, J. B. Sothers and W. Templeton, Can. J. Chem., 39, 488 (1971); G. Buchi, C. C. Inman E. S. Lipinsky, J. Am. Chem. Soc., 76, 4327 (1954); D. R. Arnold, R. L. Hinman and A. H. Glick, Tetrahedron Lett., 1425 (1964); N. C. Yang, M. Nussin, M. J. Jorgenson and S. Murov, ibid., 3657 (1964).

2. D. R. Arnold, Adv. Photochem., 6, 301 (1968).

3. S. Searles, Jr., E. F. Lutz and M. Tamres, J. Am. Chem. Soc., 82, 2932 (1960).

4. K. S. Ong and R. L. Whistler, J. Org. Chem., 37, 572 (1972).

5. N. C. Yang and W. Eisenhardt, J. Am. Chem. Soc., 93, 1277 (1971); T. Kubota, K. Shima, S. Toki and H. Sakrai, Chem. Commun., 1462 (1969).