Communications TO THE EDITOR

A New Fructose Anhydride

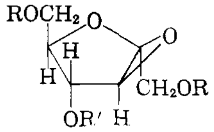
Sir:

Nitrates of ketohexoses, in contrast to aldohexoses, have not yet been obtained in the monomeric form. Schwager and Leibowitz[1] have recently shown that the nitration of fructose by means of a nitric-sulfuric acid mixture[2] affords a mixture of nitrates of difructose dianhydrides along with other dimeric derivatives of fructose. In a course of a study designed toward the formation of monomeric fructose nitrates we found that this could be achieved by using aprotic nitration agents.[3]

Nitration of fructose by means of N_2O_5 in chloroform according to the method of Caesar and Goldfrank[4] yielded a mixture of monomeric fructose nitrates. Fractional crystallization of this mixture afforded in 30% yield, long crystalline needles of a trinitrate (I), melting at 80.5° (from methanol). $[\alpha]_D^{25} = +34.5$ (ethanol). *Anal.* Calcd. for $C_6H_7O_{11}N_3$: N, 14.14; mol. wt., 297. Found: N, 14.02; mol.wt., 300 (in benzene). In the infrared spectrum I shows three absorption bands at 1665 cm.$^{-1}$; 1306 cm.$^{-1}$ and 2180 cm.$^{-1}$ (O-NO_2). λ_{max}^{EtOH} 220 mμ, log ϵ, 3.28.

Catalytic reduction of I with palladium-charcoal (10%) in ethanol, according to Kuhn[5] resulted in complete denitrification, yielding a colorless sirup (II), $[\alpha]_D^{25} = +79.4$ (ethanol). Infrared: 3366 cm.$^{-1}$, 3306 cm.$^{-1}$ (OH), 1064 cm.$^{-1}$ (C-O ethers) and 1263 cm.$^{-1}$ (epoxide). It did not respond to the Fehling test, but underwent facile acid hydrolysis in cold *N* hydrochloric acid solution affording fructose in quantitative yield, identified by its optical rotation, chromatographic R_f value and by its osazone (m.p. 207°). Acetylation of II by means of acetic anhydride–pyridine gave a crystalline triacetate (III), m.p. 112° (from ethanol), $[\alpha]_D^{25} = +57.4$ (ethanol). *Anal.* Calcd. for $C_{12}H_{16}O_8$: C, 50.00, H, 5.59; mol. wt., 288. Found: C, 49.93. H, 5.1; mol. wt., 289. Infrared: 1751 cm.$^{-1}$ (C=O), 1230 cm.$^{-1}$ (C—O ether) 1264 cm.$^{-1}$ (epoxide). II resisted oxidation by means of potassium periodate even after prolonged standing. Exhaustive methylation of II followed by acid hydrolysis afforded a sirup which failed to produce an osazone. Tritylation of II by means of trityl chloride–pyridine[6] afforded a ditrityl derivative (IV) as colorless crystals (from ethanol) melting at 207°. *Anal.* Calcd. for $C_{44}H_{38}O_5$: C, 81.88; H, 5.88. Found: C, 81.74; H, 5.74. Infrared: 3410 cm.$^{-1}$, 3370 cm.$^{-1}$ (OH), 3030 cm.$^{-1}$ (C-H), 1262 cm.$^{-1}$ (epoxide). Tosylation of I by tosyl chloride–pyridine[7] gave exclusively a ditosyl derivative (V) as colorless crystals melting at 156° (from ethanol). *Anal.* Calcd. for $C_{20}H_{22}O_9S_2$: C, 51.48; H, 4.68; S, 12.86. Found: C, 51.52; H, 4.86, S, 12.5. Infrared: 3546 cm.$^{-1}$ (OH), 1373 cm.$^{-1}$, 1184 cm.$^{-1}$ (O–SO_2) 1265 cm.$^{-1}$ (epoxide). Heating a solution of V in acetone and sodium iodide at 100° produced two molar equivalents of sodium *p*-toluenesulfonate in quantitative yield along with an iodide derivative. Nitration of II by means of N_2O_5 in $CHCl_3$ resulted in the re-formation of I while nitration by means of HNO_3–H_2SO_4 caused polymerization.

The series of reactions clearly permits the assignment of 2,3-*anhydro*-fructofuranose structure for II. For absolute configuration assignment, we studied the mechanism of formation of I and the information now at hand suggests that the epoxide ring is oriented above the furanose ring,[3] as formulated below.



I. R=R′=No$_2$. II. R=R′=H. III. R=R′=Ac. IV. R=Tr; R′=H. V. R=Ts; R′=H.

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Azomethine and α-Bromoamine Formation in the Aralkylation of Certain Weak Aromatic Amines in Dimethyl Sulfoxide[1]

Sir:

Alkylation of weak aromatic amines with alkyl bromides (*e.g.*, 2-aminofluorenone with ethyl bro-

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