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REACTION OF TETRA-O-ACYL-1-DEOXY-D-ARABINO-HEX-1-ENOPYRANOSE WITH HYDROGEN FLUORIDE. PREPARATION OF 3,4-UNSATURATED HEXOSES.

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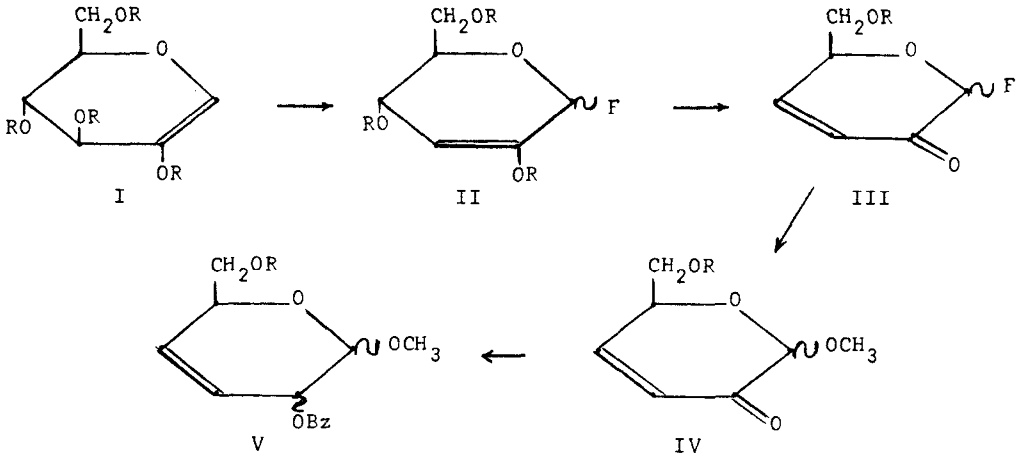
In continuation of studies of the reaction of glycal derivatives with hydrogen halides (1) the behaviour of acylated 1-deoxy-hex-1-enopyranoses towards hydrogen fluoride has now been investigated.

Treatment of tetra-O-acetyl-1-deoxy-D-arabino-hex-1-enopyranose (Ia) with anhydrous hydrogen fluoride at -70° or, alternatively, with a solution of hydrogen fluoride in benzene at +5° gave, in almost quantitative yield, the 2,3-unsaturated fluoride (IIa). When (Ia), or the corresponding tetrabenzoate (Ib), was treated with anhydrous hydrogen fluoride at -30° for 3 or 24 hours, respectively, a quantitative yield of the fluorides (IIIa) or (IIIb) were obtained. The products, (II) and (III), were isolated as rather unstable syrups which could be purified, yet with considerable losses, by preparative TLC. The 2,3-unsaturated fluoride (IIa) was obtained as a virtually homogeneous anomer which was characterized through its NMR spectrum (Table 1), very similar to that of the corresponding α-chloride (2). The enone-fluorides (IIIa) and (IIIb) both appear as mixtures of the two anomers in an α:β proportion of 10:1. In Table 1 are given NMR data of the predominant anomers which were obtained in a pure state after chromatography. Compounds similar to (III) have recently been described by Katsuhara _et al_. (3) in the ketose-series.

Treatment of crude (IIIa) or (IIIb) with one molar equivalent of methanol in methylene chloride, in the presence of a catalytic amount of BF_3, gave the corresponding methyl glycosides (IVa) and (IVb) in high yields. The products appeared as mixtures of anomers which could be separated by chromatography with some losses. Their structures were determined by NMR spectroscopy (Table 1). Compounds of the type (III) and (IV) all had IR bands at 1700-1705 cm^{-1}, characteristic of α,β-unsaturated ketones.

Ferrier _et al_. (4) have demonstrated that brief treatment of (Ia) or (Ib) with alcohols and catalytic amounts of BF_3 leads to 2,3-unsaturated glycosides. We have found that prolonged reaction of (Ia) with methanol and boron trifluoride results in the formation of (IVa). The yield was lower, however, than in the reaction proceeding _via_ the fluoride (IIIa) as described above.



a : R = Ac

b : R = Bz

TABLE 1.

Compound	Anomer	H_1	H_2	H_3	H_4	H_5	H_6	$H_{6'}$	$J_{1,F}$	$J_{3,4}$	$J_{3,5}$	$J_{4,5}$	$J_{5,6}$ c)	$J_{6,6'}$	$[\alpha]_D^{25}$	c	Yield %
II a	α	5.70		5.90	5.40	4.10 - 4.30			56.0	2.0		8.5					
II b	α	6.00		6.25	6.05	4.50 - 4.90			56.0	2.0		9.0					
III a	α	5.57		6.29	7.10	4.97	4.40	4.32	51.2	10.4	2.4	1.7	5.0	11.8	-126.9°	8.29	
III b	α	5.57		6.28	7.12	5.05	4.61	4.55	51.0	10.4	2.0	1.6	4.8	12.0	-115.6°	3.67	
IV a	α	4.80		6.17	6.97	4.76	4.35	4.29		10.7	2.5	1.8	5.0	11.6	-7.9°	3.18	53
IV a	β	4.81		6.22	7.03	4.70	4.40	4.32		10.7	2.0	3.0			-133.4°	2.07	16
IV b[a)]	α	4.81		6.20	7.05	4.85	4.60	4.51		10.7	2.6	1.5	5.0	11.4	-39.6°	1.66	52
IV b	β	4.84		6.23	7.08	4.85	4.63	4.55	$J_{1,2}$	10.3	2.0	2.9			-111.8°	3.56	15
V	α	5.28	5.60	5.80-6.10		4.40 - 4.65			4.2						-30.5°	8.49	44
V[b)]	β	4.91	5.52	6.00-6.15		4.45 - 4.75			3.0						+1.0°	2.13	45

a) mp. 85.5 - 86°

b) - 77.0 - 78°

c) In all cases $J_{5,6}$ is of the same magnitude as $J_{5,6'}$

Reduction of (IVa) or (IVb) with $LiAlH_4$, followed by acylation, yielded 3,4-unsaturated methylglycosides (V). If the reduction was carried out with anomerically pure (IVa), virtually one product resulted, indicating that the reaction proceeds stereospecifically. NMR data of the products are presented in Table 1. The configuration at C-2 has not yet been determined.

Treatment of tri-O-acyl-1-deoxy-D-*erythro*-pent-1-enopyranose, or the corresponding D-*threo* derivatives, with hydrogen fluoride or methanol in the presence of BF_3 gave results completely analogous to those described above. Details will be published elsewhere.

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