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Preliminary communication

An unusual transformation of 3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-*erythro*-hex-3-enofuranose under the action of iodine and thallous salts

AFANASSI A. AKHREM, NATALIA B. KHRIPACH, and IGOR A. MIKHAILOPULO
Institute of Bioorganic Chemistry, Byelorussian S.S.R. Academy of Sciences, 220603 Minsk (U.S.S.R.)

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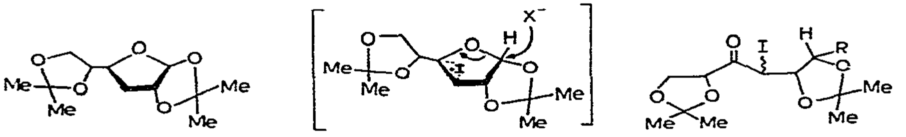
Reaction of iodine and thallium(I) fluoride, isocyanate, and acetate with 3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-*erythro*-hex-3-enofuranose[1] (1) in inert solvents (ether, benzene, carbon tetrachloride) at room temperature, afforded the acyclic ketones 3–5 in high yields. The isocyanate was converted into the methyl carbamate prior to isolation. Thus, the reaction results in the unusual opening of the furanose ring as proposed in Scheme 1.



1

2

3 R = F
4 R = NHCOOMe
5 R = OAc

Scheme 1

The fluoride 3*, prepared in anhydrous ether and isolated (80%) by crystallization from the reaction mixture, had m.p. 110–112°, $[\alpha]_D$ −92° (*c* 1, chloroform), $\nu_{max}^{CCl_4}$ 1725 cm^{-1} (C=O); no absorption in the regions 3100–3600 and 1500–1700 cm^{-1}. In the p.m.r. spectrum, the doublet of doublets ($J_{1,2}$ 1.0, $J_{1,F}$ 66 Hz) at lowest field was assigned to H-1, which is *trans* to H-2 and geminal to the fluorine[2]. A $J_{F,2}$ value of 15 Hz is consistent with the assigned structure[4–6], and the configuration of C-1 is thus *R*. The $J_{2,3}$ value of 10 Hz indicates[3] an antiperiplanar relationship of H-2 and H-3.

It is well known that reactions at C-3 of 1,2-*O*-isopropylidenealdofuranoses involve *exo* approach of reactants[7], so that the intermediate 2 is tentatively assigned the *trans*-configuration of the substituents at C-2 and C-3. Thus, compound 3 is 3-deoxy-1-fluoro-3-iodo-1,2:5,6-di-*O*-isopropylidene-D-*xylo*-hex-4-ulose. Although 3 has a negative Cotton effect (Table I) in the region of the n→π* electron transition of the carbonyl group, and the polar α-iodine atom must make a major contribution to the dichroism of the compound[8], no definitive assignment of the configuration at C-3 can be made

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*For all new compounds, satisfactory elemental analyses were obtained.

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.R. [a] AND C.D. [b] DATA

npound vent)	*Chemical shifts (p.p.m.)*				*Coupling constants (Hz)*		*C.d. [θ]* 10^{-3} *(λ nm)*
	H-1	*H-2*	*H-3*	*Others*	$J_{1,2}$	$J_{2,3}$	
D_6)	6.13q	4.84s	4.64d	1.13s 1.26s CMe_2 1.32s 1.44s	1.0	10.0	−13.3(320); 3.7(257); 0.0(390, 267, 247)
SO-d_6)	5.50q	4.50q	4.95d	1.36s CMe_2 1.50s 3.66s COOMe 8.50d NH ($J_{NH,1}$ 9.0 Hz)	5.0	10.0	−12.3(321); 9.6(263); 0.0(390, 274, 250)
l_4)	6.42d	4.85q	4.60d	1.30s 1.38s CMe_2 1.43s 1.50s 2.04s COMe	2.0	10.0	−14.6(320); 6.1(259); 0.0(375, 272, 247)
l_4)	5.90d	4.97t	4.32q	1.16s 1.18s CMe_2 1.36s 1.40s	4.5	4.5	

ectra were recorded on a Model JNM PS-100 (JEOL, Japan) spectrometer, using Me_4Si as an internal standard. ignments were made using the double-resonance technique and INDOR-method. Key: s, singlet, d, doublet, iplet, q, quadruplet. [b]C.d. curves were recorded with a JASCO Model J-20 (Japan) instrument for solutions aethanol.

this evidence because of molecular flexibility. However, examination of the most-ole conformations of the *xylo* and *ribo* iodides indicates that the negative Cotton ect is best interpreted in terms of the former configuration[9].

Reduction of 3 with sodium borohydride in anhydrous methanol at room nperature gave 3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-*xylo*-hexofuranose[10–12] 50%), thereby establishing that the configurations at C-2 and C-5 were unaltered by iodine and thallium fluoride treatment.

During the synthesis of 3, three other products were formed (t.l.c.), and one (6) isolated by column chromatography and tentatively identified as 3-deoxy-4-fluoro-odo-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose. Values for $J_{1,2}$ and $J_{2,3}$ of 4.5 (Ref. and for $J_{F,3}$ of 28 Hz[4] are consistent with this assignment.

The reaction of iodine and thallium(I) acetate with the olefin 1 gave the tate 5 as the sole product (95%), m.p. 71–72°, $[\alpha]_D$ −66.5° (*c* 0.2, chloroform), $^{l_4}_{x}$ 1755 (OAc), 1725 cm^{-1} (ketone). The corresponding isocyanate was obtained in analogous manner and treated with methanol to give the corresponding urethane (80%), p. 139–141°, $[\alpha]_D$ −73° (*c* 1, chloroform), $\nu_{max}^{CCl_4}$ 1710 and 1725 (C=O), 1515 and 50 cm^{-1} (NH).

The $J_{1,2}$ value of 5.0 Hz for the urethane raises doubts regarding the stereochemistry at C-1. Otherwise, this compound and the acetate 5 are regarded as having structures that are analogous to that of the fluoro compound 3.

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