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Preliminary communication

The Ivanov reaction of 2, 3:5, 6-di-*O*-cyclohexylidene-D-mannonolactone

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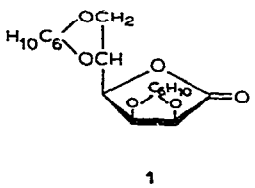
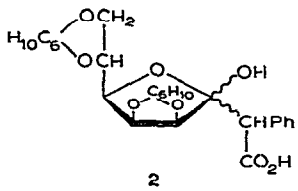
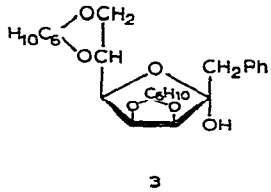
Although long-known, the Ivanov reaction[1] apparently has not yet been applied in the carbohydrate field, and we now report an application to 2, 3:5, 6-di-*O*-cyclohexylidene-D-mannono-1,4-lactone[2] (1)



1



2



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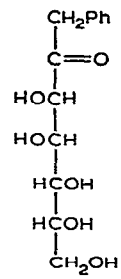

4

When the lactone 1 was heated with a five-fold excess of the Ivanov reagent, conventionally prepared by treatment of phenylacetic acid with isopropylmagnesium chloride in ether, 79% of the expected product 4,5:7,8-di-*O*-cyclohexylidene-2-deoxy-2-phenyl-D-*manno*-3-octulofuranosonic acid (2), as colourless needles, m.p. ~115° (dec.) (from benzene and then ethanol), $[\alpha]_D^{18}$ +77° (*c* 6.7, chloroform), ν_{max} 1610 (Ph), 1710 (carboxylic C=O), and 3490 cm^{-1} (OH). N.m.r. data (CH_2Cl_2): δ 1.46 (m, 20 protons, cyclohexylidene groups) and 7.1 (s, 5 protons, Ph) (Found: C, 65.96; H, 7.29. $C_{26}H_{34}O_8$ calc.: C, 65.82; H, 7.17%).

3,4:6,7-Di-*O*-cyclohexylidene-1-deoxy-1-phenyl-α-D-*manno*-2-heptulofuranose (3), a by-product (12%) formed by decarboxylation of 2, was isolated by chromatography as a colourless syrup, $[\alpha]_D^{18}$ 0° (*c* 6.3, chloroform), ν_{max} 1610 (Ph) and 3480 cm^{-1} (OH). (Found: C, 69.82; H, 8.10. $C_{25}H_{34}O_6$ calc.: C, 69.77; H, 7.91%). A 5mM solution of 3 in carbon tetrachloride showed ν_{max} for free hydroxyl at 3653 cm^{-1}, which established the α-D configuration.

Treatment of acid 2 with 20% ethanolic sodium hydroxide at room temperature gave a quantitative yield of 3. This transformation, which is similar to the reported[2,3] conversion of ethyl 2-deoxy-3-octulosonate into the respective methylketose, is a route to 1-aryl substituted methylketoses.

The unsubstituted ketose 4, obtained (50%) by hydrolysis of 3 with 80% acetic acid at room temperature, was a hygroscopic, colourless syrup, $[\alpha]_D^{18}$ -2° (*c* 3, water) (Found: C, 54.24; H, 7.05. $C_{13}H_{18}O_6 \cdot H_2O$ calc.: C, 54.17; H, 6.96%).

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