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Carbocyclization of 1,6-Anhydrides of *D*-Gulose and *D*-Idose

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Earlier we reported ($^{1-3}$) that 2,3,4-tri-*O*-methyl-1,6-anhydroglucopyranose and 2,3,4-tri-*O*-methyl-1,6-anhydrogalactopyranose react with metallic sodium in liquid ammonia with formation of phenol.

In the present article we publish the results of a further study of this interesting reaction on 1,6-anhydrides of *D*-idose and *D*-gulose. The 1,6-anhydrides studied were obtained from the corresponding hexoses by the action of dilute H_2SO_4.

In view of the absence at our disposal of pure *D*-idose and *D*-gulose, their synthesis was carried out. By the cyanohydrin synthesis from *D*-xylose (^{4}), lactone of *D*-gulonic acid was obtained in 42% yield; after recrystallization from aqueous alcohol it melted at 183–185°. Reduction of the gulonic acid lactone with 2.5% sodium amalgam gave syrupy *D*-gulose.

To obtain crystalline 1,6-anhydrogulopyranose, purification of *D*-gulose from inorganic salts proved necessary; for this purpose an aqueous solution of *D*-gulose was passed through the cation exchanger KU-1 and the anion exchanger EDE-10. On boiling a solution of pure *D*-gulose in a flask with a reflux condenser with 0.5 *N* H_2SO_4 for 20 hr, crystalline 1,6-anhydrogulopyranose was obtained (^{5}). Recrystallized three times from alcohol, it melted at 153–154°, yield 18.5%.

2,3,4-Tri-*O*-methyl-1,6-anhydrogulopyranose was obtained by us for the first time by methylation of 1,6-anhydrogulopyranose with dimethyl sulfate in 87% yield. After three recrystallizations from petroleum ether it melted at 41–42.5°,

$$[\alpha]_D^{21} = +85.7^\circ \quad (c = 11.9306,\ \text{water}).$$

Found %:	C 52.84; H 7.78; OCH_3 45.13
$C_9H_{16}O_5$. Calculated %:	C 52.94; H 7.84; OCH_3 45.58

From the reaction mixture after carrying out the cyanohydrin synthesis and isolation of the lactone of *D*-gulonic acid, *D*-idonic acid was obtained in the form of the brucine salt (^{6}). Recrystallized from methyl alcohol, the brucine salt melted at 169–170°.

Found %:	C 58.9; H 6.61; N 4.85
$C_{16}H_{11}O_7 \cdot C_{23}H_{27}N_2O_3$. Calculated %:	C 60.6; H 6.62; N 4.87

On decomposition of the brucine salt, a mixture of *D*-idonic acid and its lactone was obtained. Reduction of this mixture with 2.5% sodium amalgam gave a mixture of *D*-idose and the Na salt of *D*-idonic acid. Owing to the small yield, this mixture could not be purified. Therefore *D*-idose was obtained by us from *D*-galactose (^{7}) by the method of Sorkin and Reichstein. From α-methyl-*D*-galactoside and benzaldehyde, by shaking in the presence of anhydrous $ZnCl_2$, 4,6-benzal-α-methyl-*D*-galactoside (I) was obtained in 40% yield. After recrystallization from water and then from absolute alcohol, m.p. 167–168° (Sorkin and Reichstein give m.p. 174–176°).

Treatment of I (in absolute pyridine solution) with a solution of *p*-toluenesulfonyl chloride in chloroform and keeping the reaction mixture at 40° for 4 days gave 2,3-ditosyl-4,6-benzal-α-methyl-*D*-galactoside (II) in 93% yield.

After recrystallization from a petroleum ether—chloroform mixture, m.p. 174° (Sorkin and Reichstein: 179–180°).

$C_{28}H_{30}O_{10}S_2$.	Found, %:	C 57.5; H 5.10; S 10.82
	Calculated, %:	C 56.92; H 5.12; S 10.86

Saponification of II with a 2.7 *N* solution of sodium methoxide in methyl alcohol, with boiling of the reaction mixture for 1.5 hours, gave crystalline 2,3-anhydro-4,6-benzal-α-methyl-*D*-guloside (III), m.p. 164–177° (from a chloroform—ether mixture); yield 60%. It is possible that the product is contaminated with an admixture of 2,3-anhydro-4,6-benzal-α-methyl-*D*-taloside. Their separation was not worthwhile, since both anhydro derivatives give the same 4,6-benzal-α-methyl-*D*-idoside.

$C_{14}H_{16}O_5$.	Found, %:	C 63.58; H 6.05
	Calculated, %:	C 63.61; H 6.10

The 2,3-anhydro derivative was readily converted into 4,6-benzal-α-methyl-*D*-idoside (IV) in 71% yield by boiling in a flask with a reflux condenser with a 5% KOH solution for 20 hours. White crystals (from methanol) melted at 144–146°.

$C_{14}H_{18}O_6$.	Found, %:	C 59.86; H 6.55
	Calculated, %:	C 59.55; H 6.43

Reduction of IV with hydrogen in an autoclave at 70° and a pressure of 110 atm in the presence of Raney Ni gave α-methyl-*D*-idoside (V) in the form of a colorless syrup. On boiling V with 5% H_2SO_4 for 6 hours, neutralizing the H_2SO_4, and evaporating the aqueous solution, a syrup was obtained which crystallized on standing in a refrigerator. The crystals of 1,6-anhydroidopyranose were recrystallized from an alcohol—acetone mixture, m.p. 124–126°.

The trimethyl ether of 1,6-anhydroidopyranose has not been described in the literature. 1,6-Anhydroidopyranose was methylated twice with dimethyl sulfate. As a result, a syrup was obtained which, on distillation in vacuo, boiled at 117–119°/10 mm.

$C_9H_{16}O_5$.	Found, %:	C 52.1; H 8.15; OCH_3 45.06
	Calculated, %:	C 52.94; H 7.84; OCH_3 45.58

The resulting trimethyl ethers of 1,6-anhydroidopyranose and 1,6-anhydrogulopyranose were studied in the reaction of interaction with metallic sodium in liquid ammonia.

The conditions for carrying out the experiment were analogous to the optimal conditions established by us for trimethyllevoglucosan.

A sample of 2,3,4-tri-*O*-methyl-1,6-anhydrogulopyranose (0.005 mole) was dissolved in 20 ml of liquid ammonia, and metallic sodium (0.03 mole) was added to the solution; the sealed ampoule was kept for 8 hours at the temperature of dry ice, and then at room temperature with periodic shaking. The time for complete decolorization of the ammoniacal sodium solution varied in different experiments from 2 to 7 days.

After this the ampoule was opened, the ammonia was removed, and the residue—a white powdery substance—was decomposed with water acidified with H_2SO_4. From the acidic solution phenol was distilled off with steam. The yield of phenol in different experiments was 45–49%. In the experiment with 2,3,4-tri-*O*-methyl-1,6-anhydroidopyranose, the same ratios of reagents were maintained. After 7 days the sodium had reacted completely. The yield of phenol was 49%.

The work carried out has shown that, in the interaction reaction of 2,3,4-trimethyl ethers of 1,6-anhydrosugars with metallic sodium in liquid ammonia, cleavage of the pyranose and anhydro rings occurs, with carbocyclization followed by aromatization.

The reaction studied is apparently characteristic of the methyl ethers of all diastereoisomeric 1,6-anhydroaldohexoses.

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Note: Figure translations are in progress. See original paper for figures.