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Abstract

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CHEMISTRY

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SYNTHESIS OF SOME CARBON-CARBON DERIVATIVES OF CARBOHYDRATES

(Presented by Academician A. I. Oparin, 23 VII 1957)

As described earlier, the organomagnesium method gave good results in the synthesis of carbon–carbon derivatives of *d*-glucose, *d*-galactose, *d*-xylose, and *l*-arabinose, containing various aglycones ($^{1-4}$).

In the present work this method was applied to the preparation of several new compounds: phenyltetraacetylgalactose, *o*-tolyltetraacetylxylose, allyltetraacetylgalactose, and allyltriacetylarabinose. It was established that acetylated allyl sugars are capable of adding, at the double bond of the allyl residue, molecules of chlorine, bromine, and diiodane. Halogen derivatives of the previously synthesized phenethyltetraacetylxylose were also obtained. Acetochloromonoses, which are starting products in the synthesis of C–C derivatives of carbohydrates, were obtained by treating sugar acetates with phosphorus pentachloride and aluminum chloride in chloroform solution.

Experimental Part

The β-pentaacetates of glucose and galactose required for the work, as well as β-tetraacetate of xylose, were obtained by acetylating monosaccharides with acetic anhydride in the presence of anhydrous sodium acetate ($^{5-7}$).

α-Chlorotetraacetylglucose was obtained by the method of Hudson and Jackson (^{8}). By the same method, upon boiling sugar acetates with phosphorus pentachloride and aluminum chloride in chloroform solution, α-chlorotetraacetylgalactose (yield 79% of theoretical) and α-chlorotriacetylxylose (yield 41% of theoretical) were obtained.

β-Chlorotriacetyl-*l*-arabinose was obtained by a new procedure from *l*-arabinose in one stage, without isolation of the crystalline tetraacetate.

Preparation of β-chlorotriacetyl-*l*-arabinose. 25 g (0.166 mole) of *l*-arabinose was mixed with 20 g of anhydrous sodium acetate, 120 ml of acetic anhydride was added, and the mixture was heated on a water bath (90–100°) with an efficient reflux condenser.

After heating for 2 hours, the solution was poured, with stirring, into 500 ml of water with ice. After 2 hours the tetraacetate was extracted with 120 ml of chloroform; the extract was washed with water, with sodium bicarbonate solution, and dried over calcium chloride. The dried chloroform solution was boiled for 2 hours with 20.9 g (0.1 mole) of phosphorus pentachloride and 10 g (0.074 mole) of aluminum chloride. The solution was poured into ice water; the chloroform layer was separated, washed with sodium bicarbonate solution and with water, dried over calcium chloride, and decolorized with activated charcoal. The clear solution was diluted twofold with petroleum ether and evaporated to dryness. After removal of the solvent, β-chlorotriacetyl-*l*-arabinose was isolated as colorless crystals, m.p. 146–147°. Yield 18 g (37% of theoretical).

Phenyltetraacetylgalactose. Phenyltetraacetylgalactose was obtained by the previously proposed method for the synthesis of anisyl tetra-

acetylglucose (1) from 3.93 g (0.16 mole) of magnesium, 25.2 g (0.16 mole) of bromobenzene, and 5 g (0.0136 mole) of acetochlorogalactose.

After the usual work-up, phenyltetraacetylgalactose was isolated as a transparent thick syrup that could not be crystallized. The substance is soluble in ordinary organic solvents and insoluble in water. Yield 2.7 g (43% of theory). On oxidation of 1.2 g of the syrup, 0.22 g of benzoic acid was isolated.

The substance is described for the first time.

Found, %:	C 58.45;	H 5.70
$C_{20}H_{24}O_9$. Calculated, %:	C 58.82;	H 5.88

o-Tolyltriacetylxylose. The substance was obtained from 3.93 g (0.16 mole) of magnesium, 27.5 g (0.16 mole) of *o*-bromotoluene, and 5 g (0.0186 mole) of acetochloroxylose. *o*-Tolylacetoxylose was isolated in the usual way and purified by recrystallization from butanol. The product was obtained as colorless crystals in a yield of 2.8 g (47% of theory). M.p. 110–111°. The substance is soluble in alcohol, ether, benzene, and acetone and insoluble in water. On oxidation of the substance, phthalic acid was isolated.

The substance is described for the first time.

Found, %:	C 61.84;	H 6.30
$C_{18}H_{22}O_7$. Calculated, %:	C 61.71;	H 6.28

Dibromophenyltriacetylxylose. To a solution of 0.5 g (0.0013 mole) of previously obtained phenyltriacetylxylose (2) in 10 ml of glacial acetic acid, 1.8 g (0.011 mole) of bromine was added. After one hour the mixture was poured into water. Dibromophenyltriacetylxylose was isolated in the usual way as a colorless syrup, which crystallized on standing. After recrystallization from isopropyl alcohol, colorless crystals with m.p. 80–81.5° were obtained. Yield 0.58 g (82% of theory).

On oxidation of the substance with an alkaline solution of potassium permanganate, 3,5-dibromo-4-ethoxybenzoic acid was isolated.

The substance is described for the first time.

Found, %: Br 29.44
$C_{19}H_{21}O_8Br_2$. Calculated, %: Br 29.79

Dichlorophenyltriacetylxylose. On chlorination of 0.5 g (0.0013 mole) of phenyltriacetylxylose with a solution of 0.8 g (0.012 mole) of chlorine in 10 ml of carbon tetrachloride, dichlorophenyltriacetylxylose was obtained as a colorless noncrystallizing syrup. Yield 0.45 g (76% of theory).

The substance is described for the first time.

Found, %: Cl 15.61
$C_{19}H_{21}O_8Cl_2$. Calculated, %: Cl 16.0

Dibromoallyltriacetylxylose. 0.5 g (0.0016 mole) of previously described allyltriacetylxylose (3) was dissolved in 10 ml of acetic acid, and 1.8 g (0.011 mole) of bromine was added to the solution. After standing for one hour, the solution was poured into ice water, extracted with ether, and the ether extract was washed with a dilute alkali solution and with water and dried over calcium chloride. The residue obtained after distillation of the ether was dissolved in a small amount of hot butanol; on cooling, dibromoallyltriacetylxylose separated as colorless needles with m.p. 123–124°.

The substance is described for the first time.

Found, %: Br 34.85
$C_{14}H_{20}O_7Br_2$. Calculated, %: Br 34.79

Dibromoallyltetraacetylglucose. Bromination of 0.5 g (0.0014 mole) of allyltetraacetylglucose with a solution of bromine in glacial

acetic acid under the above-described conditions leads to the formation of dibromoallyltetraacetylglucose. After recrystallization from isopropyl alcohol, white crystals with m.p. 63.5–65° were obtained. Yield 0.57 g (80% of theoretical).

The substance is described for the first time.

Found, %: Br 29.89
$C_{11}H_{24}O_9Br_2$. Calculated, %: Br 30.07

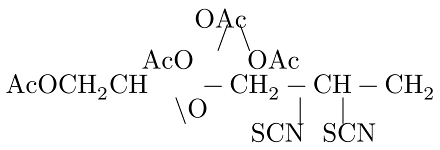
Dithiocyanatoallyltetraacetylglucose. To a solution of rhodan, prepared from 0.3 g (0.019 mol) of ammonium thiocyanate and 0.31 g of bromine in 5 ml of acetic acid, was added a solution of 0.7 g (0.0018 mol) of allyltetraacetylglucose ([1]) in 12 ml of acetic acid.

After standing in sunlight for 1 hour, the mixture was poured into water; the aqueous solution was extracted twice with ether, and the ether extract was washed with water and with soda solution and dried over calcium chloride after decolorization of the ether solution with activated charcoal. On distilling off the ether, a colorless syrup was obtained, which could be crystallized by recrystallization from isopropyl alcohol. The substance was obtained as colorless crystals with m.p. 112-113°. Yield 0.73 g (72% of theoretical). The substance is soluble in alcohol, ether, benzene, and acetone and is insoluble in water and petroleum ether.

Found, %: N 5.51; S 13.26

$C_{18}H_{24}O_9N_2S_2$. Calculated, %: N 5.73; S 13.11

Obviously, the structure of the substance may be represented by the following formula:



$$\begin{array}{l} \qquad\qquad\qquad\qquad\quad \mathrm{OAc} \\ \qquad\qquad\qquad \mathrm{AcO} \qquad \mathrm{OAc} \\ \mathrm{AcOCH_2CH} \qquad\quad - \mathrm{CH_2} - \underset{\mathrm{SCN}}{\mathrm{CH}} - \underset{\mathrm{SCN}}{\mathrm{CH_2}} \\ \qquad\qquad\qquad \backslash \mathrm{O} \end{array}$$

The substance is described for the first time.

Dithiocyanatoallyltriacetylxylose. Dithiocyanatoallyltriacetylxylose was obtained by the above-described method from 1 g (0.0032 mol) of allyltriacetylxylose and a solution of rhodan in acetic acid, in the form of pale-yellow needles, which after recrystallization from aqueous ethyl alcohol melted at 85.5–88°. Yield 1.23 g (88% of theoretical).

The substance is described for the first time.

Found, %: N 6.52; S 15.50

$C_{16}H_{20}O_7N_2S_2$. Calculated, %: N 6.72; S 15.37

The following substances were isolated in the form of noncrystallizing syrups: allyltriacetylarabinose (yield 43% of theoretical), dibromoallyltriacetylarabinose, dichloroallyltriacetylarabinose, dithiocyanatoallyltriacetylarabinose, allyltetraacetylgalactose (yield 24% of theoretical), dibromoallyltetraacetylgalactose, and dichloroallyltetraacetylglucose.

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