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Abstract

Full Text

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Yu. A. ZHDANOV and G. N. DOROFEENKO

SYNTHESES IN THE FIELD OF C–C-SUBSTITUTED CARBOHYDRATES

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As was established (ˆ1), the most convenient method for the synthesis of sugar derivatives in which the carbohydrate residue is linked by a direct carbon–carbon bond to an aglycone is the interaction of sugar acetohalides with organomagnesium compounds. This method gave satisfactory results in the synthesis of a series of derivatives of glucose, galactose, and xylose, into whose molecules various radicals were introduced (phenyl, thienyl, anisyl, tolyl, diphenyl, allyl, etc.); some of the substituted compounds obtained were subjected to further transformations by introduction of a halogen and a nitro group ($^{2-}$4).

In the present work a description is given of the synthesis of several new C–C derivatives of carbohydrates. There were obtained *o*-tolyltetraacetylglucose and its chloro- and bromo-substituted derivatives in the phenyl nucleus, *o*-chloromethylphenyltetraacetylglucose, *p*-tetraacetylglucopyranosylacetophenone, hexachlorocyclohexyltetraacetylglucose (a hexachlorane derivative of glucose), and naphthyltetraacetylgalactose.

Experimental Part

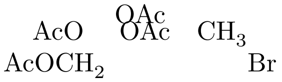
***o*-Tolyltetraacetylglucose.** To an ethereal solution of *o*-tolylmagnesium bromide, prepared in the usual manner from 3.93 g (0.16 mole) of magnesium and 27.4 g (0.16 mole) of *o*-bromotoluene, there was added a solution of 5 g (0.014 mole) of chlorotetraacetylglucose in absolute ether. The further work-up was carried out in the same way as in the synthesis of anisyltetraacetylglucose (ˆ2). As a result, 2.9 g (50% of theory) of *o*-tolyltetraacetylglucose was obtained, crystallizing in the form of white needles from isopropyl alcohol, m.p. 130–130.5°. The compound is soluble in ether, alcohol, acetone, and benzene, and insoluble in water. Destructive oxidation of *o*-tolyltetraacetylglucose with alkaline permanganate gave phthalic acid. The substance is described for the first time.

Found, %: C 59.60; H 6.20
$C_{21}H_{26}O_9$. Calculated, %: C 59.71; H 6.16

Bromotolyltetraacetylglucose. To 0.6 g (0.0014 mole) of *o*-tolyltetraacetylglucose, dissolved in 20 ml of carbon tetrachloride, there was added 0.48 g (0.003 mole) of bromine. Bromination was carried out in the presence of iodine as catalyst.

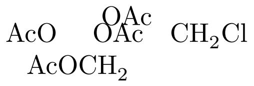
The mixture was left to stand in the dark for 4 hours and was then poured into water. The carbon tetrachloride layer was washed with water, a dilute alkali solution, and again with water, after which it was dried over calcium chloride; the solvent was distilled off under the vacuum of a water-jet pump. After removal of the solvent, 0.7 g (99% of theory) of crude bromotolyltetraacetylglucose was obtained, which after recrystallization from isopropyl alcohol was isolated in the form of colorless crystals with m.p. 109–110°. The substance is readily soluble in ordinary organic solvents and insoluble in water and petroleum ether.

In the analysis for halogen, 16.00% bromine was found in the compound (calculated 15.92%). Upon oxidation of the product with alkaline permanganate, 4-bromophthalic acid with m.p. 164–165° was obtained. The substance is described for the first time; on the basis of the halogenation conditions and the analytical data, the following structure should be assigned to it:



Chlorotolyltetraacetylglucose. 0.7 g (0.0017 mole) of *o*-tolyltetraacetylglucose was dissolved in 15 ml of carbon tetrachloride; 0.28 g of chlorine in 3.5 ml of the same solvent and a little iodine were added to the solution. The mixture was left to stand in the dark for one hour and was then treated according to the procedure described for the bromine derivative of tolyltetraacetylglucose. 0.7 g of crude product was isolated. After recrystallization from isopropyl alcohol, white crystals with m.p. 116.5–117° were obtained. Chlorotolyltetraacetylglucose is readily soluble in most organic solvents and insoluble in water and petroleum ether. Analysis found 7.86% chlorine (calculated 7.75%). Upon oxidation of the product in the usual manner, 4-chlorophthalic acid with m.p. 157° was obtained. The structure of the compound is analogous to the bromine derivative described above. The substance is described for the first time.

o-Chloromethylphenyltetraacetylglucose. 0.7 g (0.0017 mole) of *o*-tolyltetraacetylglucose was dissolved in 15 ml of carbon tetrachloride, and 0.5 g of dry chlorine dissolved in 5 ml of the same solvent was added to the solution. The mixture was left to stand in a quartz vessel in sunlight for 40 min; then, to remove chlorine and hydrogen chloride, it was washed with dilute alkali and with water. After drying over calcium chloride, the solvent was distilled off in vacuo. The residue was treated with absolute ether, which was distilled off. After evaporation of the ether, 0.65 g (90% of theory) of a colorless syrup was obtained. The product is readily soluble in organic solvents. The chlorine bound to the benzyl radical is very mobile and is quantitatively split off upon boiling with silver nitrate in methanol. Analysis found 7.95% chlorine (calculated 7.75%). The substance is described for the first time. It has the following structure:



$$\begin{array}{c} \text{OAc} \\ \text{AcO}\quad\text{OAc}\quad\text{CH}_2\text{Cl} \\ \text{AcOCH}_2 \end{array}$$

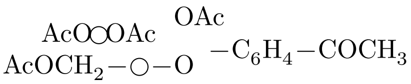
Naphthyltetraacetylgalactose*. To an ethereal solution of α-naphthylmagnesium bromide, prepared from 3.93 g (0.16 mole) of magnesium and 33.6 g (0.16 mole) of α-bromonaphthalene in 70 ml of absolute ether, was added a solution of 5 g (0.014 mole) of chlorotetraacetylgalactose in 80 ml of absolute ether. Further work-up was carried out in the usual manner. After recrystallization from isopropyl alcohol, beautiful white crystals of α-naphthyltetraacetylgalactose with m.p. 143–144° were obtained. After oxidation of the substance with alkaline permanganate, α-naphthoic acid was obtained. The substance is described for the first time.

Found, %:	C 62.75; H 5.66
$C_{24}H_{26}O_9$. Calculated, %:	C 62.89; H 5.89

* The substance was obtained jointly with V. A. Monakov.

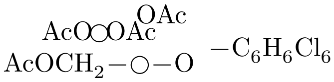
n-Tetraacetylglucopyranosylacetophenone. Into a flask equipped with a reflux condenser and dropping funnel were placed 2.5 g (0.006 mole) of phenyltetraacetylglucose and 30 ml of petroleum ether. To the resulting suspension was added 3.4 g of anhydrous aluminum chloride, and, with stirring, a solution of 1.5 g (0.012 mole) of acetyl bromide in 5 ml of petroleum ether was added dropwise. The reaction mixture was stirred for 30 min in the cold and then heated for 15 min to boiling on a water bath. To dissolve the sticky precipitate that had separated, 30 ml of dichloroethane was added, after which heating was continued for another half hour. The mixture was poured into 150 ml of water acidified with 3 ml of hydrochloric acid. The organic layer was separated, washed with water and with sodium bicarbonate solution, and then dried over calcium chloride. The solvent was distilled off in vacuo. The residue was dissolved in warm ether and decolorized with charcoal. After removal of the ether there was obtained a mixture of a liquid syrup with a crystalline substance. The latter was separated, recrystallized from isopropyl alcohol, and proved to be unreacted phenyltetraacetylglucose.

The filtrate, in an amount of 1.3 g, was a yellowish syrup with the characteristic odor of acetophenone. It is soluble in organic solvents and insoluble in water and petroleum ether. With hydrochloric 2,4-dinitrophenylhydrazine it readily forms a burgundy-red hydrazone, which melts indistinctly at 68–70°. On destructive oxidation of the product with alkaline permanganate, terephthalic acid was obtained, which indicates the following structure of the substance:



$$\begin{array}{c} \text{OAc} \\ \text{AcO}\!\bigcirc\!\!\bigcirc\!\text{OAc}\qquad -\text{C}_6\text{H}_4-\text{COCH}_3 \\ \text{AcOCH}_2-\bigcirc-\text{O} \end{array}$$

Hexachlorocyclohexyltetraacetylglucose. 1 g (0.0024 mole) of phenyltetraacetylglucose was dissolved in 20 ml of carbon tetrachloride, and a stream of dry chlorine was passed through the solution until the weight had increased by 0.9 g (0.012 mole). The reaction mixture, placed in a quartz flask, was exposed to direct sunlight and kept for 45 min. The solution was freed from hydrogen chloride and chlorine by washing with dilute alkali and water, dried, and then the solvent was distilled off. There was obtained 1.45 g (95% of theory) of a noncrystallizing yellowish syrup having a sharp terpene odor. Analysis showed 34.76% chlorine (calculated 34.29%). On prolonged standing the product darkens and decomposes with evolution of hydrogen chloride. The substance was obtained for the first time; it is a mixture of stereoisomers of the following structure:



$$\begin{array}{r} \mathrm{OAc} \\ \mathrm{AcO}\circ\circ\mathrm{OAc} \\ \mathrm{AcOCH_2}-\circ-\mathrm{O} \end{array} -\mathrm{C_6H_6Cl_6}$$

Rostov-on-Don State University
named after V. M. Molotov

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CITED LITERATURE

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

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