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Abstract

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New Carbon-Substituted Derivatives of Glucose

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Previously we synthesized various carbon-substituted derivatives of glucose, including such radicals as naphthyl, tolyl, diphenyl, thienyl, phenetyl, *p*-anisyl, and others ([1]). The general method for obtaining such compounds was organomagnesium synthesis.

The present work describes the synthesis of *o*-anisyltetraacetylglucose and its bromo and nitro derivatives. The nitro derivative of *p*-anisyltetraacetylglucose obtained by us earlier was reduced to the corresponding amine. It should be noted that the best method of reduction proved to be hydrogenation in the presence of Raney nickel; other methods (reduction with zinc, iron, tin) did not give clear results.

The synthesized 3-amino-*p*-anisyltetraacetylglucose was converted into the corresponding benzoyl and toluenesulfonyl derivatives. Its diazotized product was subjected to azo coupling with aniline, phenol, β-naphthol,

Experimental Part

** *o*-Anisyltetraacetylglucose.** To an ethereal solution of *o*-anisylmagnesium bromide, prepared from 3.93 g (0.16 mole) of magnesium and 30.62 g (0.16 mole) of *o*-bromoanisole, was added a solution of 5 g (0.014 mole) of α-chlorotetraacetylglucose in absolute ether. The mixture was heated for 5 hours on a water bath; after cooling it was decomposed with water and dilute acetic acid. The aqueous layer was separated, evaporated to dryness under reduced pressure, and acetylated with 150 ml of acetic anhydride and 5 g of anhydrous sodium acetate. The reaction mixture was poured into cold water and left until complete decomposition of the excess acetic anhydride. The solution was extracted with ether; the ethereal extract was washed with water and with sodium bicarbonate solution, dried over ignited sodium sulfate, and decolorized with animal charcoal. After evaporation of the ether, 2.44 g (42% of theory) of *o*-anisyltetraacetylglucose was obtained as a light, transparent syrup.

The substance is soluble in ether, methyl and ethyl alcohol, and acetic acid; insoluble in water. On destructive oxidation with alkaline permanganate, *o*-anisic acid was isolated. The substance is described for the first time.

structural formula

Figure 1: structural formula

$C_{21}H_{26}O_{10}$. Found %: C 57.26; H 6.33
Calculated %: C 57.53; H 5.99

5-Nitro-2-methoxyphenyltetraacetylglucose. To a solution of 13.2 g of copper nitrate trihydrate in 18.6 ml of acetic anhydride and 8 ml of acetic acid, a solution of 3 g of *o*-anisyltetraacetylglucose in 16 ml of acetic anhydride and 10 ml of acetic acid was added dropwise with shaking over the course of 30 min. The reaction mixture was heated on a water bath to 65–75°. After the reaction was complete, the mixture was poured into 400 ml of ice water with vigorous stirring. After half an hour the substance was ex-

with ether; the ether extracts were washed with sodium bicarbonate solution and water, then dried over calcium chloride. After distilling off the ether, 2.39 g (72.7% of theory) of syrupy 5-nitro-2-methoxyphenyltetraacetylglucose was obtained.

On destructive oxidation, 5-nitro-2-methoxybenzoic acid was obtained and identified. Analysis found 3.24% nitrogen (calculated 2.89%). The substance is described for the first time. Its structure is represented by the following formula:

5-Bromo-2-methoxyphenyltetraacetylglucose. To a solution of 2 g (0.0046 mole) of *o*-anisyl tetraacetylglucose in 30 ml of glacial acetic acid was added a solution of 3.75 g (0.023 mole) of bromine in 10 ml of acetic acid. The mixture was left for one hour, after which it was poured into cold water. The reaction product was extracted with ether; the ether extracts were washed with a weak alkali solution and with water, and dried with anhydrous sodium sulfate. After distilling off the ether, 1.82 g (76.7% of theory) of a syrupy product was obtained.

After recrystallization from isopropyl alcohol, 5-bromo-2-methoxyphenyltetraacetylglucose was obtained as snow-white crystals with m.p. 147–148°. The product is readily soluble in common organic solvents. Analysis for halogen found 16.19% bromine (calculated 15.47%). The substance is described for the first time.

3-Amino-*p*-anisyl tetraacetylglucose. The previously described^(2) 3-nitro-*p*-anisyl tetraacetylglucose was subjected to reduction with hydrogen in the presence of Raney nickel, which was prepared in the usual way by treating with concentrated alkali an alloy containing 40% nickel.

Into a flask equipped with a mechanical stirrer were placed 1 g each of the indicated nitro compound and Raney nickel, as well as 40 ml of water. Under ordinary conditions of temperature and pressure, hydrogen from a Kipp apparatus was passed into the reaction mixture. The reduction was completed after 6–7 hours. The solution was filtered. The precipitate was recrystallized from

structural formula

Figure 2: structural formula

structural formula: tetraacetylglucose derivative coupled through N=N to a hydroxy naphthyl group, with OCH3 substituent

Figure 3: structural formula: tetraacetylglucose derivative coupled through N=N to a hydroxy naphthyl group, with OCH3 substituent

a small amount of aqueous ethanol. The yield of substance was 0.6 g (64% of theory). The synthesized 3-amino-*p*-anisyl tetraacetylglucose is a cream-colored crystalline product with m.p. 154–157°. In determining nitrogen by Kjeldahl, 3.15% was found (calculated 3.17%). The substance is described for the first time.

The presence of the amino group was confirmed by the diazotization reaction and subsequent azo coupling. Into three test tubes were placed 0.1 g each of the obtained amine, and 3 ml of ethyl alcohol and a drop of hydrochloric acid were added to each. The mixture was cooled to 5°, after which 2–3 drops of sodium nitrite solution were added to the test tubes. Immediately thereafter, several drops, respectively, of hydrochloric-acid aniline in water, phenol in alkali, and β-naphthol in alkali were added to the test tubes containing the diazo solution. In all cases, formed···

dyes of yellow-orange color. For the latter case the structure is represented as follows:

Benzoyl-3-amino-*p*-anisyl tetraacetylglucose. 0.2 g of the initial amine was dissolved in 5 ml of dry pyridine. To the solution was added a threefold excess of benzoyl chloride (0.2 g). The mixture was allowed to stand for 4 hours, after which it was poured into water. The precipitated product was filtered off and recrystallized from ethyl alcohol. Yield 0.1 g (41.6% of theory).

The substance crystallizes as silvery scales with m.p. 162°. Analysis by the Kjeldahl method found 2.36% nitrogen (calculated 2.38%). The substance is described for the first time.

3-Toluenesulfamino-*p*-anisyl tetraacetylglucose. 0.2 g of 3-amino-*p*-anisyl tetraacetylglucose was dissolved in 5 ml of dry pyridine. To the resulting solution was added 0.2 g of *p*-toluenesulfonyl chloride. After 4 hours the mixture was poured into water taken in a large excess. The precipitated product was filtered off and recrystallized from ethyl alcohol. Yield 0.11 g (41% of theory).

The substance crystallizes as white silvery scales with m.p. 161°. Analysis by the Kjeldahl method found 2.41% nitrogen (calculated 2.41%). The substance is described for the first time. Its structure is represented by the following formula

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structural formula: tetraacetylglucose derivative bearing an OCH3-substituted cyclohexyl ring and an NHSO2-p-tolyl substituent

Figure 4: structural formula: tetraacetylglucose derivative bearing an OCH3-substituted cyclohexyl ring and an NHSO2-p-tolyl substituent

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