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Abstract

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CHEMISTRY

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SYNTHESES OF C—C DERIVATIVES OF *l*-ARABINOSE

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In earlier published works (^{1}-^{3}) we described the preparation of carbon—carbon-substituted derivatives of certain monosaccharides (glucose, galactose, xylose) by the method of organomagnesium synthesis. This route had not yet been used for the synthesis of C—C derivatives of *l*-arabinose, which is a constituent of many natural substances.

As a result of the reaction of β-chlorotriacetyl-*l*-arabinose with the corresponding Grignard reagent, we synthesized C—C-substituted derivatives of this carbohydrate containing the following radicals: phenyl, anisyl, naphthyl, phenethyl, *o*-tolyl, *p*-tolyl, thienyl, butyl. The general formula of the compounds obtained is as follows:

[[chemical structural formula: triacetylated *l*-arabinose ring with substituent R]]

On chlorination, bromination, and iodination of anisyl- and phenethylarabinose, the corresponding halogen derivatives were isolated.

Experimental Part

α-Tetraacetyl-*l*-arabinose was obtained by acetylating *l*-arabinose with acetic anhydride in the presence of sodium acetate (^{4}). For the synthesis of β-chlorotriacetyl-*l*-arabinose, 20 g (0.063 mole) of arabinose tetraacetate was dissolved in 60 ml of chloroform, and 13.1 g (0.063 mole) of phosphorus pentachloride and 5 g (0.037 mole) of aluminum chloride were added. The mixture was heated in a flask with a reflux condenser on a boiling water bath. The solution was poured into ice water; the chloroform layer was separated, washed with a solution of sodium bicarbonate and with water, dried over sodium sulfate, and decolorized with activated carbon. The clear solution was diluted twofold with normal hexane, and the solvent was slowly evaporated. A pure crystalline product with m.p. 150–152° was obtained. Yield 15–16 g (85% of theory).

Phenyltriacetyl-*l*-arabinose. To an ethereal solution of phenylmagnesium bromide, prepared from 4.08 g (0.17 mole) of magnesium and 26.7 g (0.17 mole) of bromobenzene, 5 g of chlorotriacetyl-*l*-arabinose was added in small portions. The mixture was heated on a water bath for 4 hours, poured into water, and decomposed with acetic acid. The aqueous layer was evaporated to dryness and acetylated; the reaction mixture was poured into water, extracted with ether, and the ethereal solution was washed with water and dried. After removal of the ether, 2.7 g of a light-yellow syrup was obtained, which dissolved in a small amount of butanol. On cooling, there was obtained

1.5 g of phenyltriacetyl-*l*-arabinose. On evaporation of the mother liquor, an additional 0.8 g of substance was isolated. Total yield 2.3 g (42% of theory). M.p. 91–92°. The substance is described for the first time.

Found, %: C 60.85; H 6.06

$C_{17}H_{20}O_7$. Calculated, %: C 60.71; H 5.95

o-Tolyltriacetyl-*l*-arabinose. To an ethereal solution of the Grignard reagent prepared from 3.93 g (0.16 mole) of magnesium and 27.4 g (0.16 mole) of *o*-bromotoluene was added 5 g of chlorotriacetyl-*l*-arabinose. Further work-up was carried out according to the preceding procedure. Recrystallization from butanol gave 1.9 g (33% of theory) of *o*-tolyltriacetyl-*l*-arabinose as a crystalline white powder with m.p. 99–100°. The substance is described for the first time.

Found, %: C 61.62; H 6.24

$C_{18}H_{22}O_7$. Calculated, %: C 61.72; H 6.28

p-Tolyltriacetyl-*l*-arabinose. The compound was obtained by the preceding procedure, starting from 3.5 g (0.012 mole) of acetochloroarabinose, 20.5 g (0.12 mole) of *p*-bromotoluene, and 2.8 g (0.12 mole) of magnesium. After recrystallization from butanol, 2 g (50% of theory) of *p*-tolyltriacetyl-*l*-arabinose was obtained as snow-white needles with m.p. 102–103°. The substance is described for the first time.

Found, %: C 61.66; H 6.23

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

Naphthyltriacetyl-*l*-arabinose. An ethereal solution of 3.9 g (0.013 mole) of chlorotriacetyl-*l*-arabinose was gradually added to a Grignard reagent obtained from 29 g (0.14 mole) of α-bromonaphthalene and 3.36 g (0.14 mole) of magnesium. Further work-up was carried out by the usual procedure. After recrystallization from butanol, 0.8 g (15% of theory) of white crystalline naphthyltriacetyl-*l*-arabinose was obtained with m.p. 137–138°. The substance is described for the first time.

Found, %: C 65.55; H 5.45

$C_{21}H_{22}O_7$. Calculated, %: C 65.28; H 5.69

Thienyltriacetyl-*l*-arabinose. For the synthesis of the organomagnesium compound, 25.2 g (0.12 mole) of 2-iodothiophene and 2.88 g (0.12 mole) of magnesium were taken. To the solution of the Grignard reagent was added 3.7 g (0.011 mole) of chlorotriacetyl-*l*-arabinose. By the usual procedure, after recrystallization from isopropyl alcohol, 0.8 g (20% of theory) of white crystalline thienyltriacetyl-*l*-arabinose was obtained with m.p. 96–97°. The substance is described for the first time.

Found, %: C 52.34; H 5.48

$C_{15}H_{19}O_7S$. Calculated, %: C 52.47; H 5.54

Anisyltriacetyl-*l*-arabinose. To an ethereal solution of the Grignard reagent obtained from 31.8 g (0.16 mole) of *p*-bromoanisole and 4.08 g (0.16 mole) of magnesium was added an ethereal solution of 5 g (0.016 mole) of chlorotriacetyl-*l*-arabinose. After the usual work-up and recrystallization from butanol, 2.5 g (41% of theory) of anisyltriacetyl-*l*-arabinose was obtained as glossy cream-colored needles with m.p. 153–154°. The substance is described for the first time.

Found, %: C 59.14; H 5.96

$C_{18}H_{22}O_8$. Calculated, %: C 59.01; H 6.01

Phenetyltriacetyl-*l*-arabinose. To an ethereal solution of the Grignard reagent obtained from 49 g (0.24 mole) of *p*-bromophenetole and 5.76 g (0.24 mole) of magnesium was added an ethereal solution of 7.5 g (0.026 mole) of acetochloroarabinose. After the usual work-up and recrystallization from

from butanol gave 3.6 g (38% of theory) of phenethyltriacetyl-*l*-arabinose in the form of needles with m.p. 126–127°. The substance is described for the first time.

Found, %: C 59.93; H 6.25

$C_{19}H_{24}O_8$. Calculated, %: C 60.00; H 6.32

Chloroanisyltriacetyl-*l*-arabinose. 0.5 g of anisyltriacetyl-*l*-arabinose was dissolved in 10 ml of carbon tetrachloride saturated with chlorine. After one hour the solution was poured into water; the organic layer was separated, washed with sodium bicarbonate solution, dried over anhydrous sodium sulfate, after which the solvent was distilled off. The syrupy residue was dissolved in a small amount of hot isopropyl alcohol. On cooling, 0.45 g of white crystalline chloroanisyltriacetyl-*l*-arabinose with m.p. 97–98° was obtained. The substance is described for the first time.

Found, %: C 53.64; H 5.41; Cl 8.77

$C_{18}H_{21}O_8Cl$. Calculated, %: C 53.79; H 5.48; Cl 8.84

Dichlorophenethyltriacetyl-*l*-arabinose. 0.5 g of *n*-phenethyltriacetyl-*l*-arabinose was chlorinated under the same conditions as in the preceding experiment. As a result, 0.55 g of a syrup was obtained, which could not be crystallized. In the product 15.41% chlorine was found, which corresponds to its content in dichlorophenethyltriacetyl-*l*-arabinose (calculated 15.81% chlorine). The probable structure of the product, taking into account the directing influence of the ethoxy group, is as follows:

(Figure: structural formula)

Bromoanisyltriacetyl-*l*-arabinose. 0.9 g of *n*-anisyltriacetyl-*l*-arabinose was dissolved in a mixture of 20 ml of glacial acetic acid and 3.5 g of bromine. After one hour the solution was poured into water and extracted with ether; the ether layer was washed with water and with sodium bicarbonate solution, dried, after which the ether was distilled off. After recrystallization from butanol, 0.9 g of bromoanisyltriacetyl-*l*-arabinose was obtained in the form of colorless needles with m.p. 129–130°. The substance is described for the first time.

Found, %: C 48.36; H 4.85; Br 18.08
$C_{18}H_{21}O_8Br$. Calculated, %: C 48.43; H 4.93; Br 17.97

Dibromophenethyltriacetyl-*l*-arabinose. In an analogous manner, on bromination of 0.9 g of phenethyltriacetylarabinose, 0.85 g of a noncrystallizing syrup of the dibromo derivative was obtained. In the substance 30.24% bromine was found (calculated 29.75%). The substance is described for the first time.

On iodination of the anisyl- and phenethyl-substituted arabinoses with iodine chloride, iodo derivatives were obtained in the form of syrups. Butyltriacetyl-*l*-arabinose was also obtained in the form of a noncrystallizing syrup in 63% yield.

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