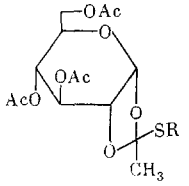
CONVERSION OF SUGAR 1,2-THIOORTHOESTERS TO BICYCLIC 1,2-ORTHOESTERS

L. V. Bakinovskii, Yu. E.Tsvetkov, N. É. Bairamova, N. F. Balan, and N. K. Kochetkov

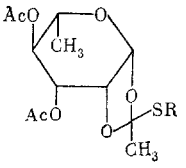
UDC 542.91:547.455

Previously we had shown that transesterification occurs when glucose ethyl thioorthoester (I) is reacted with methanol, isopropanol or 1,2,3,4-tetra-O-acetyl-β-D-glucopyranose in the presence of bases and mercury salts as the thiophilic agents, with the formation of the corresponding bicyclic glucose orthoesters [1]. This type of conversion was also realized with p-tolyl thioorthoesters of the (II) type when Raney Ni is used as the thiophilic agent, but here only ethanol and isopropanol entered into the reaction [2].

In order to study the generality of the transesterification reaction we studied the behavior of thioorthoesters, containing the S-ethyl or S-p-tolyl group, the D-glucose derivatives (I) and (II), the L-rhamnose derivatives (III) and (IV), in the reaction with partially protected monosaccharide derivatives in the presence of mercury salts.



(I), (II)



(III), (IV)

R = C_2H_5 (I), (III); p-$CH_3C_6H_4$ (II), (IV).

The thioorthoesters were synthesized under the conditions of obtaining the oxygen analogs [3], i.e., by treating aceto bromosugars with the appropriate thiol in the presence of either 2,6-lutidine or 2,4,6-collidine in nitromethane at ∿20°C, since at 40-50° are formed, besides (IV), also 2-acetoxy-3,4-di-O-acetyl-L-rhamnal and apparently p-tolylthiorhamnoside triacetate. The formation of thioglycosides in the synthesis of thioorthoesters was observed previously [4]. The structure of the rhamnal derivative followed from its PMR spectrum and a coinciding of its constants with the literature data, while the possibility of its formation under the reaction conditions was verified by running a blank experiment in the absence of p-tolyl mercaptan.

The structure of the obtained thioorthoesters was established on the basis of the elemental analysis and PMR spectral data. In contrast to the oxygen analogs, the thioorthoesters are more acid-resistant (cf. [1, 4]), but they are rapidly, in 1-2 min, hydrolyzed by $HgBr_2$ in aqueous acetone solution. Judging by the PMR spectra (Table 1), thioorthoesters (I) and (III) are pure isomers, and their CCH_3 group was assigned the endo configuration by analogy with the literature data for the oxygen 1,2-orthoesters, for which the signal of the endo-CCH_3 group is found at 1.7-1.8 ppm, while for the exo-CCH_3 group it is at ∿1.5 ppm [3, p. 114]. Thioorthoesters (II) and (IV) were obtained as a mixture of the endo and exo isomers; the main product was the endo-CCH_3 isomer, which is easily isolated by recrystallization. The formation of isomeric thioorthoesters from p-tolyl mercaptan was observed previously [4].

To study the transesterification reaction of thioorthoesters we selected some partially protected monosaccharide derivatives that contain either a primary or secondary OH group, and specifically 1,2,3,4-tetra-O-acetyl-β-D-glucopyranose, 1,2:3,4-di-O-isopropylidene-α-D-galactopyranose, 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose, 1,2-O-isopropylidene-3,6-di-O-acetyl-α-D-glucofuranose [5], and 2,3-O-isopropylidene-α-methyl-L-rhamnopyranoside [6]. The reaction of thioorthoesters (I)-(IV) with the enumerated monosaccharide derivatives was run at ∿20° by adding a solution of the thioorthoester to a solution of equimolar amounts of the hydroxyl component and heavy metal salt and a double amount of an organic base (2,6-lutidine and 2,4,6-collidine). The reaction was practically instantaneous and, based on the

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow.
Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, pp. 1905-1911, August, 1980. Original article submitted June 4, 1979.

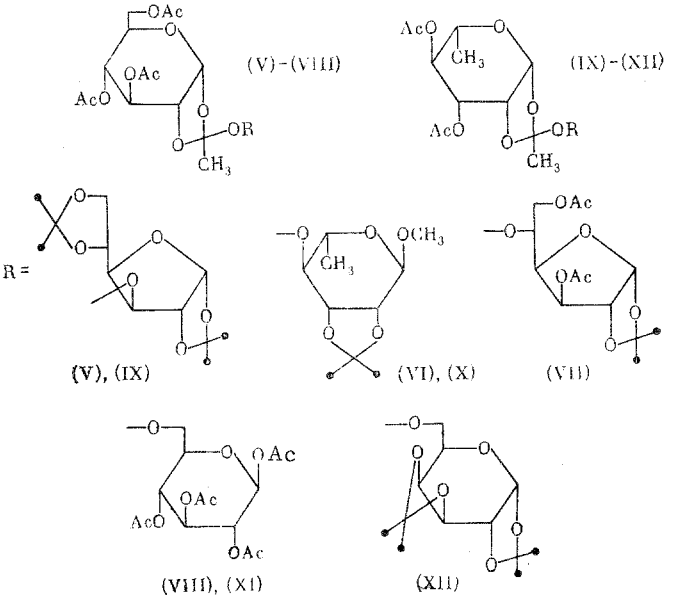
 0568-5230/80/2908-1378$07.50

TABLE 1. Characteristic Chemical Shifts in PMR Spectra of Thioorthoesters

Thioortho-ester	δ, ppm					
	CCH_3	H^1 (J, Hz)	SCH_2CH_3 (J, Hz)	SC_6H_4 (J, Hz)	OAc	other groups
(I)	1,90	5,55 (5)	1,24t 2,56 q (8)		2,00, 2,03, 2,10	
(II) endo-CCH_3*	1,72	5,68 (5)		7,05d 7,32d (8)	1,98, 1,99, 2,05	2,24 s (CH_3Ar)
(III)	1,92	5,28 (2)	1,33t 2,58q (7)		2,01, 2,06	1,20 d (J=7 Hz) (rhamnose CH_3)
(IV) endo-CCH_3	1,80	5,25 (2)		7,04 d 7,33 d (8)	1,99, 2,08	1,15 d (J=6 Hz) (rhamnose CH_3) 2,32 s (CH_3Ar)
(IV) exo-CCH_3	1,57	5,13 (2)		7,04 d 7,41 d (8)	1,96, 2,08	0,84 d (J=6 Hz) (rhamnose CH_3) 2,33 s (CH_3Ar)

*Cf. [4].

TLC data, the starting thioorthoester was absent in the reaction mixture within 1-2 min after



mixing the reactants. Besides the desired orthoester, the mixture contained the starting hydroxyl component and hydrolysis product of the thioorthoester (respectively either glucose tetraacetate or rhamnose triacetate), and also traces of thioglycosides, isomeric with the starting thioorthoesters.

The orthoesters were isolated by chromatography on a silica gel column; in the synthesis of orthoester (VII) the isolation was preceded by acetylation. In a number of cases before chromatography the diethylmercury mercaptide, which is soluble in organic solvents, was converted to HgS, since washing the reaction mixture with KI solution proved to be ineffective (test with dithizone). The obtained orthoesters (V)-(XII) were characterized by the PMR spectra, hydrolytic test [3, p. 111] under mild acid conditions, and, in some cases, by comparing the constants with those reported in the literature. The results of studying the reaction of thioorthoesters with monosaccharide derivatives are given in Table 2.

As can be seen from the data in Table 2, thioorthoesters (I) and (III), which contain an S-ethyl group, give somewhat higher yields of the orthoesters; $Hg(OCOCF_3)_2$ proved to be a more efficient thiophilic agent than $HgBr_2$. As a result, sugar 1,2-thioorthoesters can serve as convenient starting compounds for the synthesis of bicyclic sugar 1,2-orthoesters that contain the moieties of complex alcohols.

TABLE 2. Conditions of Transesterification Reaction and Yields of Orthoesters

Starting thioortho-ester	Thiophilic agent	Solvent	Ortho-ester	Yield, %*
(I)	$HgBr_2$	Nitromethane	(V)	40
	$HgBr_2$	»		50 †
	$Hg(CF_3CO_2)_2$	Benzene		55
	$AgClO_4$	Nitromethane		42
(II)	$HgBr_2$	»		41
	$Hg(CF_3CO_2)_2$	Benzene		49
(I)	$HgBr_2$	Nitromethane	(VI)	56
(I)	$HgBr_2$	»	(VII)	26
(II)	$HgBr_2$	»	(VIII)	31
(III)	$Hg(CF_3CO_2)_2$	Benzene	(IX)	33 †
(IV)	$Hg(CF_3CO_2)_2$	»	(IX)	26
(III)	$Hg(CF_3CO_2)_2$	»	(X)	47 †
	$HgBr_2$	Nitromethane	(XI)	45
(III)	$Hg(CF_3CO_2)_2$	Benzene	(XI)	55
	$Hg(CF_3CO_2)_2$	»	(XI)	58 †
(IV)	$Hg(CF_3CO_2)_2$	»	(XI)	32
(III)	$Hg(CF_3CO_2)_2$	»	(XII)	58

*Yields after chromatography and recrystallization, execpt for the syrupy (VI), (X), and (XII).

†The reaction was run in the presence of 3 Å molecular sieves.

EXPERIMENTAL

The nitromethane was vacuum-distilled (200 torr) over urea, twice over P_2O_5, and then over CaH_2; the benzene was distilled over Na; the 2,6-lutidine and 2,4,6-collidine were distilled over KOH and then over CaH_2; the TLC was run on plates covered with loose silica gel L 5/40, and the compounds were detected using aqueous $KMnO_4$ solution and 25% H_2SO_4 solution, with subsequent heating. The column chromatography was run on silica gel L100/160, using gradient elution with either benzene–ether (A) or benzene–ethyl acetate (EA) (B) mixtures in the presence of 1 vol.% of triethylamine. The solutions were evaporated in vacuo at 40°. The melting points were determined on a Kofler stand, and the optical rotation was determined on a Perkin–Elmer 141 polarimeter at 20 ± 2°. The PMR spectra were taken on either Varian DA-60-IL or Tesla BS-497 spectrometers in either $CDCl_3$ or CCl_4 solution, and using either TMS or HMDS as the internal standard.

1,2-O-(1-Ethylthioethylidene)-3,4,6-tri-O-acetyl-α-D-glucopyranose (I). To 10 g (24.4 mmoles) of acetobromoglucose in 30 ml of nitromethane were added 5.55 ml (48.8 mmoles) of 2,6-lutidine and 9.0 ml (122 mmoles) of ethyl mercaptan, and the mixture was kept for 48 h. The excess mercaptan was removed in vacuo, and the residue was diluted with 70 ml of a 1:2 chloroform–hexane mixture and washed with water (3 × 50 ml). The organic layer was filtered through a silica gel bed (2-3 cm), and the filtrate was evaporated and chromatographed on column A. We obtained 6.8 g (71%) of (I) as a syrup, $[\alpha]_D$ +32.1° (C 1.2, $CHCl_3$). Found: C 49.52; H 5.97; S 8.47%. $C_{16}H_{24}O_9S$. Calculated: C 48.98, H 6.12; S 8.16%.

1,2-O-(1-Ethylthioethylidene)-3,4-di-O-acetyl-β-L-rhamnopyranose (III). To a solution of 3.8 g (11 mmoles) of acetobromorhamnose in 10 ml of nitromethane were added 2.5 ml (20 mmoles) of 2,4,6-collidine and 3 ml (50 mmoles) of ethyl mercaptan, and the mixture was kept for 10 days at ∿20°. The excess mercaptan was removed in vacuo, and the residue was dissolved in 10 ml of pyridine and treated with 5 ml of Ac_2O. After 16 h the mixture was treated with 5 ml of methanol, kept for 1 h, and then concentrated in half. The solution was diluted with 50 ml of a 1:2 chloroform–hexane mixture, washed with water (3 × 50 ml), and the organic layer was separated and evaporated. The residue was evaporated twice with heptane and chromatographed on column A. The chromatographically homogeneous product was recrystallized from petroleum ether to give 1.56 g (47%) of (III), mp 89-90°, $[\alpha]_D$ +46.7° (C 1.35, $CHCl_3$). Found: C 50.48; H 6.54; S 9.37%. $C_{14}H_{22}O_7S$. Calculated: C 50.29; H 6.63; S 9.58%.

1,2-O-(1-p-Tolylthioethylidene)-3,4,6-tri-O-acetyl-α-D-glucopyranose (II). To a solution of 8.22 g (20 mmoles) of acetobromoglucose in 20 ml of nitromethane were added 2.48 g

(20 mmoles) of p-tolyl mercaptan and 2.75 ml (20.8 mmoles) of 2,4,6-collidine. The mixture was stirred in a N_2 stream for 8 h at 35°, let stand at ~20° for 48 h and then 100 ml of ether was added. The precipitate of collidine hydrobromide (3.73 g, 92%) was filtered and the filtrate was evaporated. The residue was dissolved in a mixture of 120 ml of benzene and 20 ml of ether, and the solution was passed through a small bed of silica gel and evaporated. After recrystallization from alcohol we obtained 4.6 g (51%) of (II), mp 115-116°, $[\alpha]_D$ +81.4°, $[\alpha]_D$ +82.6° (C 0.5, $CHCl_3$); cf. [4]. Judging by the TLC data, the mother liquor contains (II), its exo-CCH_3 isomer, and p-tolylthioglucoside tetraacetate.

1,2-O-(1-p-Tolylthioethylidene)-3,4-di-O-acetyl-β-L-rhamnopyranose (IV). a) To a solution of 3.69 g (10.5 mmoles) of acetobromorhamnose in 5 ml of nitromethane were added 2.9 ml (21.8 mmoles) of 2,4,6-collidine and 1.3 g (10.5 mmoles) of p-tolyl mercaptan. The mixture was stirred at 40-50° in a N_2 stream for 5 h, let stand overnight at 20°, and then heated again for another 5 h at 50° until the starting bromide had disappeared (checked by TLC in a 9:1 benzene—EA system). To the cooled reaction mixture was added 50 ml of ether, the collidine hydrobromide precipitate (1.65 g, 81%) was separated, and the filtrate was evaporated. The residue was dissolved in ether, washed with water (3 × 40 ml), dried over $MgSO_4$, and the solution was evaporated. After recrystallization from an ether—petroleum ether mixture was obtained 1.36 g of (IV), mp 141-142° (from alcohol), $[\alpha]_D$ +113° (C 1.13, $CHCl_3$). Found: C 57.26; H 6.12; S 8.09%. $C_{19}H_{24}O_7S$. Calculated: C 57.55; H 6.10; S 8.08%.

The mother liquor was evapoated, and the residue (2.1 g) was chromatographed on column B. We isolated an additional 0.38 g of (IV) (total yield 41.0%), 50 ml of mixed endo- and exo-CCH_3 isomers, and 350 mg of a mixture that contained, besides the exo isomer of (IV) (R_f 0.65, 9:1 benzene—ethyl acetate), presumably p-tolylthiorhamnoside triacetate (R_f 0.55) and 2-hydroxyrhamnal triacetate (R_f 0.45). The last mixture was rechromatographed (column B) to give 80 mg (2.8%) of 2,3,4-tri-O-acetyl-1,5-anhydro-6-desoxy-L-arabino-hexen-1-ite (2-hydroxy-L-rhamnal acetate), mp 74.5-75.5° (from ether—petroleum ether), $[\alpha]_D$ +65° (c 0.2, $CHCl_3$). The mixed melting point with an authentic sample (see below) is not depressed. PMR spectrum (δ, ppm): 6.55 s (1H, H^1), 5.47 d (1H, J = 4.5 Hz, H^3), 4.99 dd (1H, J = 4.5 and 6 Hz, H^4), 4.18 m (1H, H^5), 2.10, 2.06 and 2.03, 3s (9H, CH_3CO), 1.34 d (3H, J = 7.5 Hz, C^6H_3).

b) A solution of 17.1 g (50 mmoles) of acetobromorhamnose in ~20 ml of nitromethane was treated with 6.2 g (50 mmoles) of p-tolyl mercaptan and 13.2 ml (100 mmoles) of 2,4,6-collidine for 48 h at 20°, and then worked up as indicated above. Recrystallization from 80 ml of alcohol gave 7.38 g of (IV), mp 142-143°. From the mother liquor by chromatography were isolated an additional 1.82 g of (IV) (total yield 46%) and 1.49 g (7.5%) of the exo isomer of (IV), mp 79.5-80.5° (from ether—petroleum ether), $[\alpha]_D$ +161° (C 1.33, $CHCl_3$). Found: C 57.60; H 6.21; S 8.12%. $C_{19}H_{24}O_7S$. Calculated: C 57.55; H 6.10; S 8.08%.

2,3,4-Tri-O-acetyl-1,5-anhydro-6-desoxy-L-arabino-hexen-1-ite. To 1.05 g (3 mmoles) of acetobromorhamnose in 4 ml of nitromethane were added 630 mg (3.2 mmoles) of collidine hydrobromide and 0.44 ml (3.3 mmoles) of collidine, and the mixture was stirred for 20 h at 50°. To the cooled mixture was added 20 ml of ether, the precipitate was filtered, the filtrate was evaporated, and the residue was chromatographed on column B. We obtained 300 mg (37%) of syrupy product. After recrystallization first from an alcohol—ether—heptane mixture and then from an ether—heptane mixture we obtained the crystalline 2-hydroxy-L-rhamnal acetate, mp 71-72°, $[\alpha]_D$ +66° (C 0.56, $CHCl_3$). From [7]: mp 74°, $[\alpha]_D$ +65°; from the D-enantiomer, mp 72-74°, $[\alpha]_D$ −66° [8].

Test for Thioorthoesters. To a solution of 3-5 mg of the thioorthoester in 0.5 ml of acetone was added 0.5 ml of a 1% $HgBr_2$ solution in 95% aqueous acetone. After 1-2 min 1 drop of pyridine was added, the solution was evaporated to dryness, and the residue was dissolved in $CHCl_3$ and analyzed by TLC. Thioorthoesters (I)-(IV) are completely hydrolyzed under these conditions and the reaction mixture contains only products with a much smaller R_f value, corresponding to either D-glucose tetraacetate or L-rhamnose triacetate.

1,2-O-[1-O-(1,2:5,6-Di-O-isopropylidene-α-D-glucofuranosyl-3)-ethylidene]-3,4,6-tri-O-acetyl-α-D-glucopyranose (V). a) To a suspension of 200 mg (0.55 mmole) of $HgBr_2$ in 7 ml of nitromethane were added 145 mg (0.56 mmole) of 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose and 0.065 ml (0.57 mmole) of 2,6-lutidine. With stirring, a solution of 220 mg (0.56 mmole) of thioorthoester (I) and 0.065 ml of lutidine in 5 ml of nitromethane was added in drops over 20 min. Then 0.5 ml of pyridine was added to the reaction mixture and a H_2S stream was passed through until all of the mercury was precipitated (test with dithizone). The precipitate was filtered, the filtrate was evaporated, and the residue was chromatographed on column A.

We obtained 160 mg (48.5%) of (V), which, after recrystallization from an ether–petroleum ether mixture gave 130 mg (40%) of (V) with mp 110-112°, $[\alpha]_D$ −9° (C 1.4, $CHCl_3$); cf. [9].

b) The reaction was run the same as in Expt. a) using 115 mg (0.56 mmole) of $AgClO_4$ (without the H_2S treatment), and after chromatography and recrystallization we obtained 140 mg (42%) of (V), which was identical with that described above.

c) To a solution of 240 mg (0.92 mmole) of 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose, 390 mg (0.92 mmole) of $Hg(OCOCF_3)_2$ and 0.105 ml (0.92 mmole) of 2,6-lutidine in 10 ml of benzene was added in drops, with stirring, a solution of 360 mg (0.92 mmole) of thioorthoester (I) and 0.105 ml of lutidine in 6 ml of benzene over 20 min. After treatment with H_2S as described in Expt. a), chromatography, and recrystallization, we obtained 300 mg (55%) of (V).

d) To a solution of 260 mg (1 mmole) of 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose and 0.115 ml (1 mmole) of 2,6-lutidine in 10 ml of nitromethane were added 360 mg (1 mmole) of $HgBr_2$ and 0.5 g of ignited ground 3 Å molecular sieves. The mixture was stirred for 1 h and then a solution of 390 mg (0.99 mmole) of thioorthoester (I) and 0.115 ml of 2,6-lutidine in 7 ml of nitromethane was added in drops. The mixture was filtered and worked up the same as in Expt. a). After chromatography and recrystallization we obtained 290 mg (50%) of (V), identical with that described above.

e) A solution of 130 mg (0.5 mmole) of 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose was treated with thioorthoester (II) (227 mg, 0.5 mmole) in the presence of 0.115 ml (1 mmole) of 2,6-lutidine and 180.5 mg (0.5 mmole) of $HgBr_2$ in 5 ml of nitromethane. The mixture was diluted with 10 ml of ether, filtered, and the filtrate was evaporated. After chromatography on column A and recrystallization we isolated 120 mg (40.6 g) of (V).

f) A mixture of 260 mg (1 mole) of 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose and 454 mg (1 mole) of thioorthoester (II) was reacted in the presence of 426 mg (1 mmole) of $Hg(OCOCF_3)_2$ and 0.264 ml (2 mmoles) of 2,4,6-collidine in 5 ml of benzene. After chromatography on column A and recrystallization we obtained 290 mg (49%) of (V).

1,2-O-[1-O-(2,3-O-Isopropylidene-α-methyl-L-rhamnopyranosidyl-4-)ethylidene]-3,4,6-tri-O-acetyl-α-D-glucopyranose (VI). Using the method described for the preparation of orthoester (V), from 110 mg (0.51 mmole) of 2,3-O-isopropylidene-α-methyl-L-rhamnopyranoside and 200 mg (0.51 mmole) of thioorthoester (I) in the presence of 180 mg (0.5 mmole) of $HgBr_2$ and 0.12 ml (1.1 mmoles) of 2,6-lutidine in 12 ml of nitromethane we obtained 180 mg (56%) of (VI) as a colorless syrup, $[\alpha]_D$ +8.7° (C 1.3, $CHCl_3$). PMR spectrum (δ, ppm): 5.74 d (1H, J = 5 Hz, H^1 of glucose moiety), 4.83 s (1H, H^1 of rhamnose), 3.66 s (3H, CH_3O), 2.10 s (9H, $3CH_3CO$), 1.82 s (3H, CCH_3 of orthoester), 1.56 and 1.34, 2 s (6H, isopropylidene), 1.26 d (3H, J = 5 Hz, CCH_3 of rhamnose).

1,2-O-[1-O-(1,2-O-Isopropylidene-3,6-di-O-acetyl-α-D-glucofuranosyl-5-)ethylidene]-3,4,6-tri-O-acetyl-α-D-glucopyranose (VII). For reaction we took 390 mg (1.27 mmoles) of 1,2-O-isopropylidene-3,6-di-O-acetyl-α-D-glucofuranose, 500 mg (1.27 mmoles) of thioorthoester (I) in the presence of 460 mg (1.27 mmoles) of $HgBr_2$ and 0.3 ml (2.6 mmoles) of 2,6-lutidine in 15 ml of nitromethane. The reaction mixture was filtered, the filtrate was evaporated, 5 ml of pyridine and 2 ml of Ac_2O were added, and the whole was let stand overnight. Then 5 ml of alcohol was added to the reaction mixture, after 1 h 50 ml of $CHCl_3$ was added, and the whole was washed with water (5 × 20 ml). The organic layer was evaporated, the residue was dissolved in 15 ml of $CHCl_3$, 0.2 ml of Et_3N was added, and an H_2S stream was passed through until the test with dithizone was negative. After separating the precipitate the filtrate was evaporated and chromatographed on column A. After recrystallization from alcohol we obtained 210 mg (26%) of (VII), mp 172-174°, $[\alpha]_D$ +7.2° (C 2.1, $CHCl_3$); cf. [10].

1,2-O-[1-O-(1,2,3,4-Tetra-O-acetyl-β-D-glucopyranosyl-6)ethylidene]-3,4,6-tri-O-acetyl-α-D-glucopyranose (VIII). Using the conditions for the preparation of orthoester (V), from 174 mg (0.5 mmole) of 1,2,3,4-tetra-O-acetyl-β-D-glucopyranose, 227 mg (0.5 mmole) of thioorthoeseter (II), 180.5 mg (0.5 mmole) of $HgBr_2$, and 0.115 ml (1 mmole) of 2,6-lutidine in 4 ml of nitromethane, after chromatography on column A and recrystallization from alcohol, we obtained 110 mg (31.5%) of (VIII), mp 130-141°, $[\alpha]_D$ +29.1° (C 1.1, $CHCl_3$); cf. [1].

1,2-O-[1-O-(1,2:5,6-Di-O-isopropylidene-α-D-glucofuranosyl-3)ethylidene]-3,4-di-O-acetyl-β-L-rhamnopyranose (IX). a) Using the conditions for the preparation of orthoester (V), from 260 mg (1 mmole) of 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose, 334 mg (1 mmole) of thioorthoester (III), 426 mg (1 mmole) of $Hg(OCOCF_3)_2$, 0.3 ml (2.3 mmoles) of 2,4,6-collidine, and 0.5 g of 3 Å molecular sieves in 10 ml of benzene we obtained 180 mg (33%) of (IX),

mp 154-155° (from $CHCl_3$—petroleum ether), $[\alpha]_D$ −6.4° (C 1, $CHCl_3$). Found: C 54.65; H 6.78%. $C_{24}H_{36}O_{13}$. Calculated: C 54.15; H 6.81%. PMR spectrum (δ, ppm): 1.24 d (3H, J = 7 Hz, CCH_3 of rhamnose), 1.30, 1.33, 1.40 and 1.48, 4 s (12H, two isopropylidene groups), 1.76 s (3H, CCH_3 of orthoester), 2.03 and 2.08, 2 s (6H, $2CH_3CO$).

b) Using the same conditions, from 200 mg (0.5 mmole) of (IV) we obtained 26% of (IX).

1,2-O-[1-O-(2,3-O-Isopropylidene-α-methyl-L-rhamnopyranosidyl-4)ethylidene]-3,4-di-O-acetyl-β-L-rhamnopyranose (X). Using the conditions for the preparation of orthoester (V), from 334 mg (1 mmole) of thioorthoester (III), 218 mg (1 mmole) of 2,3-O-isopropylidene-α-methyl-L-rhamnopyranoside, 426 mg (1 mmole) of $Hg(OCOCF_3)_2$, 0.3 ml (2.3 mmoles) of 2,4,6-collidine, and 0.5 g of 3Å molecular sieves in 10 ml of benzene we obtained 230 mg (47%) of (X), syrup, $[\alpha]_D$ −18.4° (C 2.47, $CHCl_3$). Found: C 53.39; H 7.04%. $C_{22}H_{34}O_{12}$. Calculated: C 53.78; H 6.99%. PMR spectrum (δ, ppm): 1.20 d (6H, J = 7 Hz, CCH_3 of rhamnose), 1.28 and 1.46, 2 s (6H, isopropylidene), 1.72 s (3H, CCH_3 of orthoester), 2.03 and 2.07, 2 s (6H, CH_3CO), 3.30 s (3H, CH_3O).

1,2-O-[1-O-(1,2,3,4-Tetra-O-acetyl-β-D-glucopyranosyl-6)ethylidene]-3,4-di-O-acetyl-β-L-rhamnopyranose (XI). a) Using the conditions for the preparationof orthoester (V), from 167 mg (0.5 mmole) of thioorthoester (III), 174 mg (0.5 mmole) of 1,2,3,4-tetra-O-acetyl-β-D-glucopyranose, 180 mg (0.5 mmole) of $HgBr_2$, and 0.11 ml (1 mmole) of 2,6-lutidine in 5 ml of nitromethane we obtained 145 mg (45%) of orthoester (XI), mp 162-164° (from $CHCl_3$—petroleum ether), $[\alpha]_D$ +21.9° (C 2.2, $CHCl_3$). Found: C 50.26; H 5.84%. $C_{26}H_{36}O_{17}$. Calculated: C 50.31; H 5.84%. PMR spectrum (δ, ppm): 1.26 d (3H, J = 7 Hz, CCH_3 or rhamnose), 1.72 s (3H, CCH_3 of orthoester), 2.00, 2.02, and 2.12, 4 s (18H, CH_3CO), 5.65 d (1H, J = 8 Hz, H^1 of glucose).

b) The transesterification of 167 mg (0.5 mmole) of thioorthoester (III) under the same conditions, but in the presence of 213 mg (0.5 mmole) of $Hg(OCOCF_3)_2$ in 5 ml of benzene gave 170 mg (55%) of (XI), identical with that described above.

c) The transesterification of thioorthoester (III) the same as described in b), but with the addition of molecular sieves, gave orthoester (XI) in 58% yield.

d) To a solution of 310 mg (0.9 mmole) of acetobromorhamnose in 1 ml of nitromethane were added 0.3 ml (2.3 mmoles) of 2,4,6-collidine and 310 mg (0.89 mmole) of 1,2,3,4-tetra-O-acetyl-β-D-glucopyranose, and the mixture was kept for 48 h at ∿20°. Then 3 ml of pyridine and 1.5 ml of Ac_2O were added, the mixture was kept for 16 h at ∿20°, 1.5 ml of methanol was added, and after 1 h the mixture was evaporated. The residue was dissolved in 10 ml of $CHCl_3$, the solution was washed with water (5 × 10 ml), the organic layer was evaporated, and the residual pyridine was distilled off with heptane. After recrystallization from a $CHCl_3$—ether mixture we obtained 320 mg (60%) of orthoester (XI), identical with that described above.

e) Using method c) for the preparation of orthoester (V), the reaction was run with 270 mg (0.78 mmole) of 1,2,3,4-tetra-O-acetyl-β-D-glucopyranose, 300 mg (0.75 mmole) of thioorthoester (IV), 0.18 ml (1.36 mmoles) of 2,4,6-collidine, and 322 mg (0.75 mmole) of $Hg(OCOCF_3)_2$ in 5 ml of benzene. After chromatography on column A and recrystallization from $CHCl_3$—ether-heptane mixture we obtained 150 mg (32%) of orthoester (XI), identical with that described above.

1,2-O-[1-O-(1,2,3,4-Di-O-isopropylidene-α-D-galactopyranosyl-6)ethylidene]-3,4-di-O-acetyl-β-L-rhamnopyranose (XII). Using method c) for the preparation of orthoester (V), from 260 mg (1 mmole) of 1,2:3,4-di-O-isopropylidene-α-D-galactopyranose, 334 mg (1 mmole) of thioorthoester (III), 0.22 ml (2 mmoles) of 2,6-lutidine, and 426 mg (1 mmole) of $Hg(OCOCF_3)_2$ in 10 ml of benzene, after chromatography on column A, we obtained 310 mg (58%) of syrupy orthoester (XII), $[\alpha]_D$ −30.8° (C2, $CHCl_3$). Found: C 54.89; H 6.95%. $C_{24}H_{36}O_{13}$. Calculated: C 54.15; H 6.81%. PMR spectrum (δ, ppm): 1.24 d (3H, J = 7 Hz, CCH_3 of rhamnose), 1.28, 1.39 and 1.50, 3 s (12H, two isopropylidene groups), 1.68 s (3H, CCH_3 of orthoester), 2.00 and 2.08, 2 s (6H, CH_3CO).

CONCLUSIONS

1. The synthesis of some 1,2-O-(1-ethylthio- and p-tolylthio)ethylidene derivatives of D-glucose and L-rhamnose was described.

2. The reaction of sugar thioorthoesters with monosaccharide derivatives, containing one hydroxyl group, in the presence of mercury salts and an organic base, gives bicyclic sugar orthoesters.

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