Dioxolanylium Ions Derived from Carbohydrates. IX.

Rearrangement between Dioxolanylium and Dioxanylium Ions

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The formation of 4,6-acetoxonium and benzoxonium ion derivatives of methyl gluco-, manno-, galacto- and idopyranosides from the 6-azido-6-deoxy compounds on treatment with nitrosonium ion is described and the formation and rearrangement of the 3,5-benzoxonium ion derived from methyl α-D-xylofuranoside discussed.

In previous papers of this series dealing with the rearrangement between acyloxonium ions fused to a carbohydrate molecule, neighbouring group participation from an acyl group attached to the terminal hydroxymethylene group was observed in only two cases. Thus the 2,6-dibenzoate of the 3,4-benzoxonium ion derivative of methyl α-D-altropyranoside rearranged to a 4,6-benzoxonium ion derivative of methyl α-D-idopyranoside,[1] analogously to the type of rearrangement observed by Paulsen[2] for fully acetylated hexopyranoses. Also, the 2,3-benzoxonium ion derived from methyl β-D-ribofuranoside 5-benzoate was attacked at C-5 by tosylate ion to give the 5-O-tosylate of methyl α-D-xylofuranoside 2,3-dibenzoate, the attack occurring on a small amount of 3,5-benzoxonium ion in equilibrium with the 2,3-benzoxonium ion, the only species actually observed in the solution.[3] Though in principle possible in many other cases, rearrangements between 3,4- and 4,6-acyloxonium ions have not been observed. Two explanations can be visualized: (i) an unfavourable position of the equilibrium, resulting in a concentration of 4,6-acyloxonium ion too low for direct spectroscopic observation as well as for detection through reaction with a nucleophile and (ii) an

energy barrier too high for equilibration under experimental conditions compatible with the carbohydrate part of the molecule. The present paper deals mainly with the preparation of a number of 4,6-acyloxonium ions *trans* fused to a hexopyranose ring with a view to studying their stability and rearrangements.

The method employed so far for the formation of benzoxonium ions at a specific position in carbohydrate molecules, namely oxidation of a benzaldehyde acetal with trityl carbonium ions, cannot be used to prepare 4,6-benzoxonium ions, since this reaction is strictly limited to acetals of the 1,3-dioxolane type. Therefore a new approach, based on placing a good leaving group (*i.e.* a potential carbonium ion) at C-6 subject to attack from an acyloxy group at C-4, was sought. Treatment of aliphatic azides with nitrosonium ion has been studied in detail by Doyle,[4-6] and proceeds with the loss of nitrous oxide and nitrogen to give carbonium ions which then undergo further reactions. This reaction is a most attractive prospect for the formation of acyloxonium ions since: (i) it proceeds rapidly in acetonitrile at room temperature, *i.e.* under the conditions normally employed when studying carbohydrate acyloxonium ions, (ii) the leaving group breaks down to gaseous species, nitrogen and nitrous oxide, insoluble in acetonitrile and (iii) no nucleophiles are formed in the process.

When methyl 6-azido-2,3,4-tri-O-benzoyl-6-deoxy-α-D-idopyranoside (*1*) (Scheme 1) was treated with nitrosonium hexafluorophosphate in acetonitrile at 0 °C, an instantaneous gas evolution took place and the previously described[1]
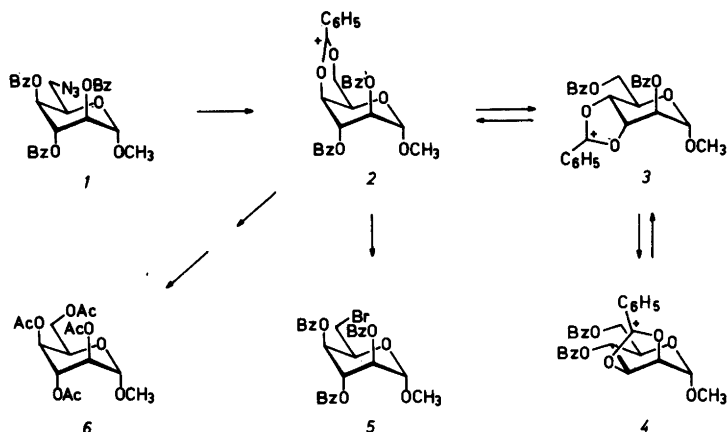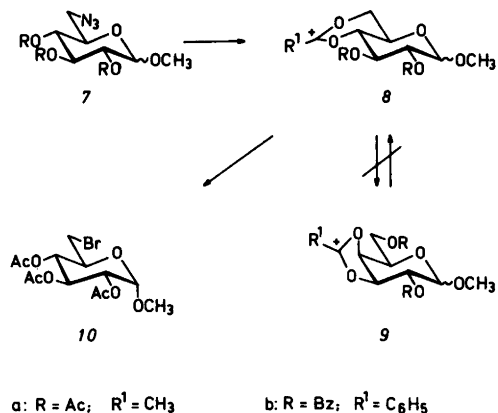
Scheme 1.

4,6-dioxanylium ion 2 was produced as seen from the ^{1}H and ^{13}C NMR spectra. Hydrolysis followed by debenzoylation and reacetylation gave methyl α-D-idopyranoside tetraacetate (6). Reaction of the dioxanylium ion 2 with bromide ion gave methyl 2,3,4-tri-O-benzoyl-6-bromo-6-deoxy-α-D-idopyranoside (5) by regiospecific attack at the primary carbon atom.

If the ido-benzoxonium ion 2, formed as described above, is left at room temperature, a rearrangement takes place to give the altro- and manno-benzoxonium ions, 3 and 4. Equilibrium is reached in ca. 1 h and if the progress of the reaction is followed by NMR spectroscopy, the altro- and manno-ions are found to be present throughout the reaction in exactly the same ratio as found in the final equilibrium mixture, suggesting that the equilibration between the dioxolanylium ions is much faster than the equilibration between the dioxolanylium ion and the dioxanylium ion. This difference in the rate of equilibration was previously suspected in view of the outcome of the reaction between the equilibrium mixture 2⇌3⇌4 and bromide ion.[1]

Treatment of methyl 2,3,4-tri-O-acetyl-6-azido-6-deoxy-α-D-glucopyranoside (α-7a) (Scheme 2) with nitrosonium ion in acetonitrile solution results in instantaneous gas evolution, and the appearance of a singlet at δ 2,67 in the ^{1}H NMR spectrum shows that an acetoxonium ion (α-8a) has been formed. Hydrolysis after 5 min at 0 °C followed by acetylation gives methyl α-D-glucopyranoside tetraacetate. Treatment of the

acetoxonium ion α-8a with bromide ion gives methyl 2,3,4-tri-O-acetyl-6-bromo-6-deoxy-α-D-glucopyranoside (10). Both of these experiments and the ^{1}H and ^{13}C NMR spectra (Tables 1 and 2) are in agreement with the formation of an acetoxonium ion fused 4,6- to the α-D-glucopyranoside. When the 4,6-acetoxonium ion α-8a is left at room temperature for 24 h no rearrangement to a 3,4-acetoxonium ion (α-9a) with galacto-configuration takes place in spite of the fact that the acetoxy-group at C-4 in α-8a is placed in a position trans to the acetoxonium ion, a situation which normally leads to equilibration. When the ion α-8a is hydrolyzed after 24 h at room temperature and deacetylated, the product

a: R = Ac; R[1] = CH₃   b: R = Bz; R[1] = C₆H₅

Scheme 2.

Table 1. ¹H NMR spectra of benzoxonium ions in acetonitrile-d_3 solution.

Compound	Chemical shifts (δ-values)									Coupling constants (Hz)							Frequency MHz
	H1	H2	H3	H4	H5	H6	H6'	CH₃C⁺	OCH₃	J_{12}	J_{23}	J_{34}	J_{45}	J_{56}	$J_{56'}$	$J_{66'}$	
α-8a	5.08	5.04	5.59	4.86	4.60	5.22	4.82	2.67	3.46	3.7	9.5	9.8	9.8	5.2	10.5	10.5	270
α-8b	5.38	5.58	6.15	5.34	4.91	5.50	5.11		3.54	3.6	9.8	10.1	9.8	5.3	10.6	10.7	270
α-12a	4.88	5.35	5.39	5.05	4.60	5.20	4.88	2.67	3.46	1.6	3.4	10.3	9.7	5.4	10.6	10.7	270
α-12b	5.15	5.86	5.94	5.67	4.93	5.49	5.26		3.56	1.7	3.3	10.4	9.8	5.5	10.6	10.7	270
α-15a	5.02	5.11	5.57	5.44	4.78	5.01		2.76	3.47	3.5	10.6	3.3	<3	<3	<3		270
α-15b	5.27	5.51	6.16	5.89	5.02	5.29			3.54	3.5	10.5	3.1	<3	<3	<3		90
β-15b	5.08	5.51	6.04	5.89	5.00	5.34			3.51	8.0	9.9	3.1		<3	<3		90
20	5.58	6.37	6.31	5.08	4.70				3.42	4.2	7.8	3.0	~4				270

is methyl α-D-glucopyranoside containing ca. 10 % of the β-anomer, showing that some anomerization takes place, due to the acidic environment. When the reaction is carried out with the benzoate α-7b the corresponding benzoxonium ion α-8b is formed. The benzoxonium ion possesses a somewhat better stability and can be followed spectroscopically for 3 d at room temperature; qualitatively, with the same result as was found for the acetates.

When methyl 2,3,4-tri-O-acetyl-6-azido-6-deoxy-β-D-glucopyranoside (β-7a) is treated with nitrosonium ion in acetonitrile at 0 °C the transitory existence of the 4,6-acetoxonium ion (β-8a) can be observed in the ¹H NMR spectrum. Hydrolysis of the reaction mixture after 5 min, followed by acetylation, gives a mixture of methyl glucopyranoside tetraacetates (α/β=15/85). When left at room temperature for 45 min the initially formed acetoxonium ion anomerizes to the α-compound (α-8a) described above. Work-up as described above now reveals that the methyl α-D-glucopyranoside predominates (75/25). After 24 h at room temperature, work-up gives methyl α- and β-D-glucopyranoside in a ratio of 90/10, reflecting the anomeric equilibrium composition for 4,6-acetoxonium ions 8a, but also showing that in this case, as in the case of the α-anomer, no equilibration takes place between the 4,6-dioxanylium ion 8 and the previously described[7] 3,4-dioxolanylium ion (9) with the galacto configuration.

Reactions between methyl 6-azido-6-deoxy-α-D-mannopyranoside triacetate (11a) and tribenzoate (11b) (Scheme 3) and nitrosonium hexafluorophosphate proceed as found for the glucosides with formation of the 4,6-acyloxonium ion (12) as seen from the ¹H and ¹³C NMR spectra. Hydrolysis followed by deacylation gives methyl α-D-mannopyranoside. When left for 24 h at room temperature the 4,6-acetoxonium ion shows no tendency to rearrange to the 3,4-acetoxonium ion (13) with the talo-configuration, since hydrolysis followed by deacylation gives a reaction mixture containing only methyl α-D-mannopyranoside and no methyl α-D-talopyranoside.

A common feature of the 4,6-acyloxonium ions with the gluco- and manno-configurations is that the oxygen atoms at C-3 and C-4 are in a diequatorial arrangement which, with the carbohydrate in the $^4C_1$ conformation, precludes

Table 2. [13]C chemical shifts (δ-values, 22.63 MHz) of benzoxonium ions in acetonitrile solution.

Compound	C1	C2	C3	C4	C5	C6	OCH₃	C⁺
α-8a	97.4	69.4[a]	65.6[a]	80.0[a]	55.8[a]	74.4[a]	54.9	187.7
α-8b	98.0	70.8	67.5	80.4	56.9	74.7	55.4	177.4
α-12a	99.6	66.1[a]	69.1[a]	79.7[a]	57.2[a]	74.4[a]	55.1	188.4
α-12b	99.5	67.1	69.8	79.7	57.7	74.3	55.2	177.7
α-15a	96.5	65.4[a]	64.0[a]	81.0[a]	56.5[a]	74.8[a]	54.6	187.4
α-15b	97.5	67.6	66.0	81.8	58.0	75.4	55.6	177.5
β-15b	100.9	68.6	69.4	80.8	61.8	75.4	56.7	
20	100.0	87.3	91.4	78.2	62.2		54.9	

[a] Assignment by analogy to the corresponding benzoates, which were assigned by selective decouplings.


a: R = Ac; R¹ = CH₃   b: R = Bz; R¹ = C₆H₅
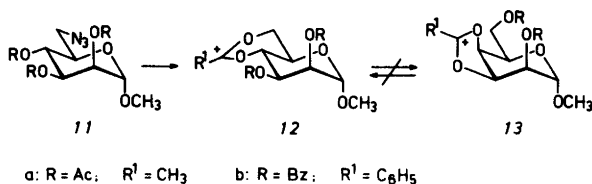
Scheme 3.

attack from the acyloxygroup at C-3 taking place from a direction opposite to the C-4−O-4 direction. For rearrangement to take place, the pyranose ring must adopt a boat conformation, but even then the *trans* fusion between the dioxanylium ion and the pyranose ring decreases the flexibility of the conformation, causing some strain if O-3 and O-4 are to adopt a *trans* diaxial arrangement. The combined effect of the required conformational shift and the strain involved in reaching C-4 from the backside are probably jointly responsible for the failure of the rearrangement to the 3,4-acyloxonium ion in case of the mannose and glucose derivatives. None of these restrictions apply to the *ido* acyloxonium ion *2,* for which the *trans* diaxial arrangement between O-3 and O-4 allows unhindered approach by the acyloxy-group at C-3 to the back of C-4, and where the *cis* fused ring system retains most of the flexibility of the pyranose ring.

When methyl 6-azido-6-deoxy-α-D-galactopyranoside triacetate (*α-14a*) or tribenzoate (*α-14b*) (Scheme 4) was treated with nitrosonium hexafluorophosphate in acetonitrile at 0 °C, gas evolution took place and the corresponding 4,6-acyloxonium ions (*α-15a* and *α-15b*) were formed as apparent from the ¹H and ¹³C NMR

spectra. Hydrolysis of the acetoxonium ion *α-15a* after 5 min at 0 °C followed by reacetylation gave methyl α-D-galactopyranoside tetraacetate. Treatment of *α-15a* with bromide ion gave methyl 6-bromo-6-deoxy-α-D-galactopyranoside triacetate (*17a*). Both results are in agreement with the formation of a 4,6-acyloxonium ion. The diox-

a: R = Ac; R¹ = CH₃   b: R = Bz; R¹ = C₆H₅
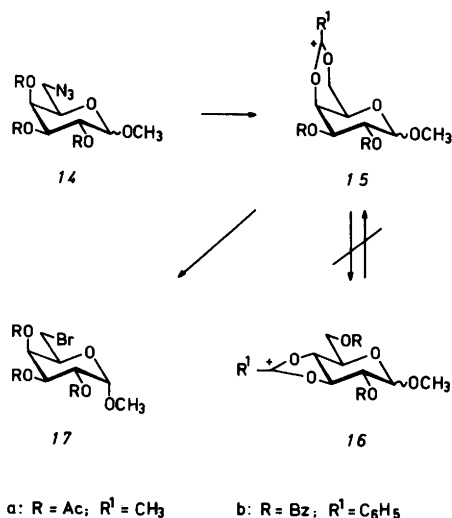
Scheme 4.

anylium ions did not show any tendency to undergo rearrangement after 24 h at room temperature, a behavior closely resembling that of dioxolanylium ions fused to pyranose rings not undergoing rearrangement through participation of *cis* vicinal acyloxy groups. When methyl 6-azido-6-deoxy-β-D-galactopyranoside tribenzoate (*β-14b*) was treated with nitrosonium ion the 4,6-benzoxonium ion (*β-15b*) was again formed as seen from the ^{1}H and ^{13}C NMR spectra and from the formation of methyl β-D-galactopyranoside after hydrolysis and deacylation. After 24 h at room temperature the dioxanylium ion *β-15b* anomerized to the α-anomer *α-15b* (90 %), but no other rearrangements were observed, the remaining 10 % being methyl β-D-galactopyranoside.

In order to test if acyloxonium ions fused 3,5 to furanose rings could be prepared from the 5-azides, a number of derivatives of 5-azido-5-deoxy-xylo- and ribofuranose were treated with nitrosonium ion. In all cases a reaction took place, but in the case of ribofuranose derivatives, for which an initially formed 3,5-acyloxonium ion would be *trans* fused to the furanose ring, complicated mixtures of short-lived acyloxonium ions resulted as seen from the NMR spectra and these reactions were not investigated further. When methyl 5-azido-2,3-di-*O*-benzoyl-5-deoxy-α-D-xylofuranoside (*18*) (Scheme 5) was treated with nitrosonium hexafluorophosphate the reaction led to only one product, methyl 5-*O*-benzoyl-2,3-benzoxonium-α-D-ribofuranoside (*20*) as seen from the ^{1}H and ^{13}C NMR spectra and from work-up (hydrolysis and deacylation) to methyl α-D-ribofuranoside. This outcome of the reaction shows that the *cis* fused 3,5-benzoxonium ion is formed readily but rearranges through neighbouring group participation from the *trans* situated 2-*O*-benzoyl group to give the observed 2,3-benzoxonium ion of *ribo* configuration.

In summary, the results obtained allow the following conclusions: the occasional failure of
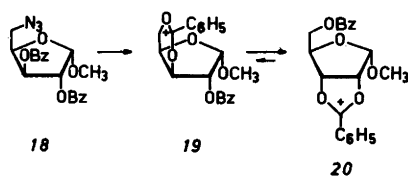
neighbouring group participation from an acyloxy group at C-6 in the hexopyranoside is not due to instability of the resulting *trans* fused 4,6-dioxanylium ion, but rather to a prohibitively high energy barrier separating the 4,6- and the 3,4-acylxonium ions; neighbouring group participation takes place in the normal manner, when the resulting 4,6-dioxanylium ion is *cis* fused to the pyranose ring. Or, put differently: a dioxanylium ion, 4,6-fused to a pyranose ring, undergoes rearrangement only with a *trans* vicinal, axially oriented neighbouring acyloxy group. This behavior is distinctly different from that prevailing in dioxolanylium ions fused to a pyranose ring, for which rearrangement takes place with any *trans* vicinal neighbouring group, irrespective of orientation.

EXPERIMENTAL

Thin layer chromatography (TLC) was performed on silica gel PF$_{254}$ (Merck), and for preparative work 1 mm layers were used on 20×40 cm plates. Melting points are uncorrected. Optical rotations were measured in chloroform solution on a Perkin-Elmer 141 instrument. ^{1}H NMR spectra were recorded on Bruker HXE 90 and HX 270 instruments and ^{13}C NMR spectra on a Bruker WH 90 instrument. All NMR spectra were measured in deuteriochloroform unless otherwise specified.

Methyl 6-azido-2,3,4-tri-O-benzoyl-6-deoxy-α-D-idopyranoside (1). Methyl 2,3,4-tri-*O*-benzoyl-6-bromo-6-deoxy-α-D-idopyranoside[1] (10.0 g) was stirred with sodium azide (10.0 g) in DMF (250 ml) at 90 °C for 4 h. Dilution with water (500 ml) and extraction with dichloromethane gave a crude product which was crystallized from ether to give 5.2 g of *1*, m.p. 130−132 °C. Two recrystallizations from ethyl acetate−pentane gave 4.0 g (43 %), m.p. 134−135 °C, $[\alpha]_D^{25}$ +51° (*c* 1.2, CHCl$_3$). Anal. C$_{28}$H$_{25}$N$_3$O$_8$: C, H, N. ^{1}H NMR (90 MHz): δ 4.99 (H1), 5.18 (H2), 5.53 (H3), 5.20 (H4), 4.60 (H5), 3.67 (H6), 3.33 (H6′), 3.57 (OCH$_3$); J_{12}, J_{13}, J_{45}~1 Hz, J_{23}, J_{34}~3, J_{56}=8.6, $J_{56'}$=4.0, $J_{66'}$=12.6.

Methyl 6-azido-2,3,4-tri-O-benzoyl-6-deoxy-α-D-mannopyranoside (11b). Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-p-toluenesulfonyl-α-D-mannopyranoside[8] (5.6 g) was stirred with sodium azide (5.6 g) in DMF (100 ml) at 90 °C for 6 h. Dilution with water (5 vol) and extraction with ether gave 3.8 g (84 %) of *11b*, m.p. 111−112 °C (from ether−pentane), $[\alpha]_D^{25}$ −93° (*c* 1.0, CHCl$_3$). Anal. C$_{28}$H$_{25}$N$_3$O$_8$: C, H, N. ^{1}H NMR (90 MHz):

Scheme 5.

δ 4.98 (H1), 5.66 (H2), 5.8 (H3, H4), 4.23 (H5), 3.52 (H6), 3.46 (H6′), 3.54 (OCH₃); J_{12}=1.6 Hz, J_{23}=3.0, J_{45}=9.7, J_{56}=5.5, $J_{56'}$=4.0, $J_{66'}$=13.

Methyl 6-azido-2,3,4-tri-O-benzoyl-6-deoxy-α-D-galactopyranoside (α-14b). Methyl 6-azido-6-deoxy-α-D-galactopyranoside [9] (438 mg) was benzoylated with benzoyl chloride (1 ml) in pyridine (10 ml) to give 993 mg (94 %) of sirupy *α-14b*. Preparative TLC (ethyl acetate—pentane 1:3) gave $[\alpha]_D^{20}$+245° (*c* 0.6, CHCl₃). Anal. C₂₈H₂₅N₃O₈: C, H, N. ¹H NMR (90 MHz): δ 5.32 (H1), 5.67 (H2), 5.96 (H3), 5.86 (H4), 4.39 (H5), 3.57 (H6) 3.31 (H6′), 3.53 (OCH₃); J_{12}=3.5 Hz, J_{23}=10.1, J_{34}=3.2, J_{45}=1.3, J_{56}=8.2, $J_{56'}$=4.1, $J_{66'}$=12.9.

Methyl 6-azido-2,3,4-tri-O-benzoyl-6-deoxy-β-D-galactopyranoside (β-14b). Methyl 2,3,4-tri-O-benzoyl-6-O-p-toluenesulfonyl-β-D-galactopyranoside [10] (3.4 g) and sodium azide (3.4 g) in DMF (50 ml) was stirred at 120 °C for 5 h. Dilution with water and extraction with ether gave 2.2 g (68 %) of *β-14b*, m.p. 120—122 °C (from ethanol). Two recrystallizations from ethanol gave m.p. 121—123 °C, $[\alpha]_D^{20}$ +209° (*c* 1.2, CHCl₃). Anal. C₂₈H₂₅N₃O₈: C, H, N. ¹H NMR (90 MHz): δ 4.72 (H1), 5.78 (H2), 5.53 (H3), 5.80 (H4), 4.11 (H5), 3.64 (H6), 3.27 (H6′), 3.61 (OCH₃); J_{12}=7.7 Hz, J_{23}=10.1, J_{34}=3.3, J_{45}=1.0, J_{56}=8.1, $J_{56'}$=3.9, $J_{66'}$=13.0.

Methyl 5-azido-2,3-di-O-benzoyl-5-deoxy-α-D-xylofuranoside (18). To methyl 2-O-benzoyl-α-D-xylofuranoside [11] (4.8 g) in pyridine (30 ml) was added 4.3 g of p-toluenesulfonyl chloride in small portions under cooling in ice–water. The reaction mixture was allowed to reach room temperature overnight, worked up and benzoylated with benzoyl chloride in pyridine in the usual manner to give 5.6 g of crude methyl 2,3-di-O-benzoyl-5-O-p-toluenesulfonyl-α-D-xylofuranoside (21), m.p. 68—73 °C (from ether). 1.0 g of *21* in 25 ml DMF was stirred with 1.0 g of sodium azide at 90 °C for 6 h. Dilution with water and extraction with ether gave 0.8 g of sirupy *18*. Preparative TLC (ether—pentane 1:1) gave $[\alpha]_D^{20}$ +249° (*c* 2.4, CHCl₃). Anal. C₂₀H₁₉N₃O₆: C, H, N. ¹H NMR (90 MHz): δ 5.39 (H1), 5.46 (H2), 5.97 (H3), 4.64 (H4), 3.5 (H5), 3.44 (OCH₃); J_{12}=4.5 Hz, J_{23}=4.5, J_{34}=6.7, J_{45}~5.

Reactions between azides and nitrosonium hexafluorophosphate

General procedure: 500 mg of the azide was dissolved in acetonitrile (dried over 3A molecular sieves), cooled to 0 °C, and nitrosonium hexafluorophosphate (~500 mg) was added in small portions during 1 min. The reaction mixture was stirred at the temperature and for the time specified under the individual compounds below. Addition of saturated aqueous sodium hydrogencarbonate and extraction with dichloromethane yielded a crude product, which was either deacylated with sodium methoxide in methanol to the methyl glycoside or reacylated with acetic anhydride or benzoyl chloride in pyridine to the peracetylated or perbenzoylated methyl glycoside.

Methyl 6-azido-2,3,4-tri-O-benzoyl-6-deoxy-α-D-idopyranoside (1). 434 mg of *1* gave after 5 min at 0 °C methyl α-D-idopyranoside of >95 % purity as seen from a ¹³C NMR spectrum.[12] Acetylation with acetic anhydride in pyridine gave 160 mg of methyl α-D-idopyranoside tetraacetate, m.p. 105—106 °C (from ether), identical (mixed m.p. 104—106 °C) with an authentic sample.

Methyl 2,3,4-tri-O-acetyl-6-azido-6-deoxy-α-D-glucopyranoside (α-7a). 500 mg of α-7a [14] gave after 30 min at 0 °C, work-up and acetylation 473 mg (90 %) of methyl α-D-glucopyranoside tetraacetate, pure (>95 %) as judged by its ¹³C NMR spectrum.[15] Crystallization from ethanol gave m.p. 99—101 °C, undepressed on admixture of a commercial sample (Koch-Light).

In another experiment the acetoxonium ion α-8a (from 500 mg of α-7a) was left over night at room temperature, and after work-up deacetylated to give 132 mg (47 %) of a mixture of methyl α- and β-D-glucopyranoside (10:1) as shown by ¹³C NMR.[13]

Methyl 2,3,4-tri-O-acetyl-6-azido-6-deoxy-α-D-mannopyranoside (11a). 536 mg of *11a* gave after 30 min at 0 °C, work-up, deacetylation and crystallization from ethanol 100 mg of methyl α-D-mannopyranoside, m.p. 186—188 °C undepressed on admixture of a commercial sample (Senn Chemicals).

In another experiment the acetoxonium ion from 520 mg of *11a* was left overnight at room temperature. Work-up and deacetylation gave 137 mg of crude methyl α-D-mannopyranoside pure (>95 %) as judged by its ¹³C NMR spectrum.[12] Crystallization from ethanol gave m.p. 186—188 °C.

Methyl 2,3,4-tri-O-acetyl-6-azido-6-deoxy-α-D-galactopyranoside (α-14a). 502 mg of α-14a gave after 15 min at 0 °C, work-up and acetylation 482 mg (92 %) of methyl α-D-galactopyranoside tetraacetate (22), which was crystallized from ether to give 390 mg of 22, m.p. 83—85 °C (lit.[16] 86—87 °C). The ¹H NMR spectrum showed that the mother liquors contained >90 % of 22.

Methyl 2,3,4-tri-O-acetyl-6-azido-6-deoxy-β-D-glucopyranoside (β-7a). 520 mg of β-7a gave after 5 min at 0 °C, work-up and acetylation 537 mg

(98 %) of a mixture of methyl α- and β-D-glucopyranoside tetraacetates (15:85) as determined by ^{13}C NMR.[12]. Two crystallizations from ethanol gave methyl β-D-glucopyranoside, m.p. 102–104 °C (lit.[17] 104 °C).

In another experiment the acetoxonium ion β-8a was left for 45 min at room temperature prior to work-up and acetylation. Again the resulting product contained (^{13}C NMR) the methyl α- and β-D-glucopyranoside tetraacetates (75:25).

In a third experiment the acetoxonium ion β-8a from 500 mg of β-7a was left at room temperature overnight. Work-up and acetylation gave 344 mg of a reaction mixture consisting of 75 % of methyl α- and β-D-glucopyranoside tetraacetates in a ratio of 90:10. 25 % of the total glycoside mixture was a new compound, identified (^{13}C NMR[18]) after deacetylation as methyl β-D-glucofuranoside.

Methyl 6-azido-2,3,4-tri-O-benzoyl-6-deoxy-β-D-galactopyranoside (β-14b). 513 mg of β-14b gave after 5 min at 0 °C, work-up and debenzoylation 161 mg (86 %) of crystalline (m.p. 169–171 °C, lit.[19] 178–180 °C) methyl β-D-galactopyranoside, pure (>95 %) according to the ^{13}C NMR spectrum.[12]

In another experiment the benzoxonium ion β-15b from 505 mg of β-14b was left at room temperature overnight prior to work-up and debenzoylation. ^{13}C NMR now showed the product (157 mg) to be a mixture of the methyl α- and β-D-galactopyranosides (90:10).

Methyl 5-azido-2,3-di-O-benzoyl-5-deoxy-α-D-xylofuranoside (18). 485 mg of 18 gave after 15 min at 0 °C, work-up and debenzoylation 125 mg (58 %) of a sirup containing 95 % methyl α-D-ribofuranoside and 5 % of the β-anomer as seen from the ^{13}C NMR spectrum.[18]

Reactions between acyloxonium ions and bromide ion

General procedure: 500 mg of the azide was dissolved in acetonitrile (dried over 3A molecular sieves), cooled to 0 °C and nitrosonium hexafluorophosphate (~500 mg) was added in small portions (~1 min). After stirring for 5 min at 0 °C 0.5 g of tetraethylammonium bromide was added and stirred for an additional h at 0 °C. Addition of saturated sodium hydrogencarbonate and extraction with dichloromethane yielded a crude product containing substantial amounts of tetraethylammonium hexafluorophosphate, which was removed by dissolution in water and re-extraction with ether (3×100 ml). The final purification by crystallization or preparative TLC is described under the individual compounds.

Methyl 2,3,4-tri-O-benzoyl-6-bromo-6-deoxy-α-D-idopyranoside (5). 537 mg of 1 gave 496 mg of crude 5, which was recrystallized from ethanol to give 276 mg (48 %) of 5, m.p. 165–166 °C showing no depression on admixture of an authentic sample.[1] Preparative TLC (ethyl acetate–pentane 1:1) of the mother liquors gave further 41 mg of 5 and two slower moving products (33 and 11 mg, respectively) tentatively identified (NMR) as the methyl 2,3,6- and 2,3,4-tri-O-benzoyl-α-D-idopyranosides, resulting from hydrolysis of the 4,6-benzoxonium ion.

Methyl 2,3,4-tri-O-acetyl-6-bromo-6-deoxy-α-D-glucopyranoside (10). 515 mg of α-7a gave 345 mg of crude 10. Preparative TLC (ethyl acetate–pentane 1:1) gave 130 mg (23 %) of 10, m.p. 118–120 °C (from ethanol, lit.[20] m.p. 117 °C). ^{1}H NMR (90 MHz): δ 4.99 (H1), 4.88 (H2), 5.49(H3), 4.97 (H4), 4.08 (H5), 3.46 (H6), 3.40 (H6′); J_{12}=3.5 Hz, J_{23}=9.5, J_{34}=8.8, J_{45}=9.7, J_{56}=3.3, $J_{56'}$=6.4, $J_{66'}$=11.0.

Methyl 2,3,4-tri-O-benzoyl-6-bromo-6-deoxy-α-D-galactopyranoside (17a). 504 mg of α-14a gave 540 mg of crude 17a, which on preparative TLC (ether–pentane 4:1) gave 428 mg of α-17a as a sirup.[14] Deacetylation with sodium methoxide in methanol and benzoylation with benzoyl chloride in pyridine gave 406 mg (49 %) of 17a, m.p. 122–123 °C (lit.[21] m.p. 122–123 °C).

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