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REACTIONS OF PHENYL CHLOROSULFATE AT OH-2 AND OH-3 OF ALDOHEXOPYRANOSE DERIVATIVES. COMPETING SUBSTITUTION AND DISPLACEMENT REACTIONS

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ABSTRACT

Reactions of phenyl chlorosulfate–sodium hydride with methyl 4,6-*O*-benzylidenealdohexopyranosides are characterized by a variety of nucleophilic substitution and displacement processes involving OH-2 and -3 of the glycosides. Depending on such factors as the relative rates of substitution of these two hydroxyl groups and their configurations, as well as temperature and stoichiometry, the products may be mono- or di-phenylsulfates (or both), 2,3-cyclic sulfates, or 2,3-oxiranes. For example, in the reaction of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside with two equivalents of phenyl chlorosulfate at +25°, the products were the 2,3-disulfate (10%), 2,3-cyclic sulfate (77%), and 2,3-*allo* epoxide (4%), whereas, at −25°, by far the major product was the 2-phenylsulfate (79%). Intramolecular displacement was so readily facilitated in the reaction of methyl 4,6-*O*-benzylidene-α-D-altropyranoside that the only products obtained were the 2,3-anhydro-*manno*- (major) and -*allo*-pyranosides. Conformations of the 2,3-cyclic sulfates are considered on the basis of their n.m.r. characteristics.

INTRODUCTION

The base-catalyzed reaction of phenyl chlorosulfate with an appropriately substituted sugar derivative provides[1–3] a means for the synthesis of a sugar sulfate through the intermediacy of a protected organosulfate. Although both primary and secondary phenylsulfates may be synthesized in this manner, primary hydroxyl groups are the more reactive. For example, in the presence of sodium hydride at −30°, methyl 2,3-di-*O*-benzyl-α-D-glucopyranoside gives[4] a 75% yield of the 6-(phenylsulfate); at room temperature, an intramolecular displacement ensues, leading to the formation of the 4,6-cyclic sulfate. In the present article, reactions at OH-2 and -3 of 4,6-*O*-benzylidenealdohexopyranoside derivatives are examined.

RESULTS AND DISCUSSION

In the presence of sodium hydride, phenyl chlorosulfate is far more highly

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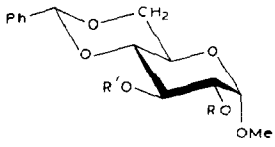
TABLE I

REACTIONS OF PHENYL CHLOROSULFATE WITH METHYL 4,6-*O*-BENZYLIDENE-α-D-GLUCOPYRANOSIDE

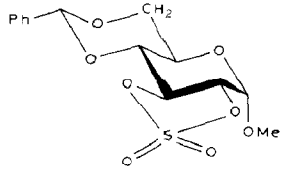
Temperature (°C)	*Time (h)*	*Reagent (mol. equiv.)*[a]	*Products (% yield)*				
			2,3-Di-(phenylsulfate)	*2-(Phenylsulfate)*	*2,3-Cyclic sulfate*	*2,3-allo-anhydride*	*Unreacted*
+50	0.5	2	10		46	15	5
	0.5	1	9		25	22	6
+25	2	2	10		77	4	4
	2	1	2		33	28	30
0	12	2	24	58	5		6
	12	1	5	59	26		4
−25	72	2	2	68	5		14
	90	1	4	60	7		25

[a]Mol of phenyl chlorosulfate/mol of D-glucoside.

regioselective for OH-2 than OH-3 of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside (**1**). Over the temperature range of −25° to 0°, yields of the 2-(phenylsulfate) (**2**) were 58–68% (see Table I), whereas the 3-substituted derivative was not detected. At room temperature and above, however, OH-3 appeared to participate in an intramolecular reaction, or to be substituted. That is, the 2,3-cyclic sulfate (**5**)* was produced in yields varying from 25 to 77% (See Table I), presumably because of an attack by the O-3 anion on the sulfur atom of **2**, and displace-



1 R = R′ = H
2 R = $PhOSO_2$, R′ = H
3 R = H, R′ = $PhOSO_2$
4 R = R′ = $PhOSO_2$



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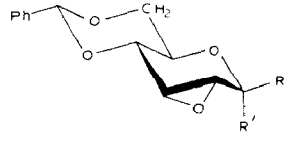
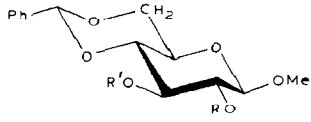
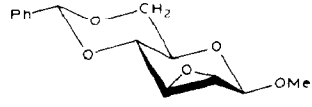


6 R = H, R′ = OMe
7 R = OMe, R′ = H



8 R = R′ = H
9 R = $PhOSO_2$, R′ = H
10 R = H, R′ = $PhOSO_2$
11 R = R′ = $PhOSO_2$



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*The synthesis of **5** represents an alternative route to cyclic derivatives of this type, prepared previously[5] by use of sulfuryl chloride.

TABLE II

REACTIONS OF PHENYL CHLOROSULFATE WITH OTHER METHYL 4,6-*O*-BENZYLIDENE-D-ALDOHEXOPYRANOSIDES

Isomer	*Temperature (°C)*	*Time (h)*	*Reagent (mol. equiv.)*[a]	*Products (% yield)*				
				2,3-Di-(phenyl-sulfate)	*Mono-(phenyl-sulfate)*	*2,3-Cyclic sulfate*	*2,3-Anhydride*	*Unreacted*
β-gluco	−20	24	2				23[b], 21[c]	50
	−10	320	2	13			43[b], 34[c]	2
	+25	48	2				43[b], 29[c]	20
			1				27[b], 25[c]	40
α-galacto	−40	240	2	39	18[d], 8[e]			30
			1	21	23[d], 10[e]			44
	−20	96	2	52	19[d], 17[e]			2
	+25	2	1	34		8	17[f]	34
			2	73		15	6[f]	4
β-galacto	−25	24	1	4	26[e]			32
		60		7	23[e]			33
		24	2		71[e]			18
	+25	2	2				69[f]	25
		2	1				43[f]	26
α-altro	−20	60	2				13[b], 49[c]	24
	0	8	2				11[b], 83[c]	4
	+25	7	2				6[b], 75[c]	4
			1				4[b], 77[c]	4
α-manno	−25	20	2	19		74		4
	+25	2	2	10		82		6

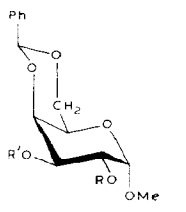
[a]Mol of phenyl chlorosulfate/mol of glycoside. [b]*allo*. [c]*manno*. [d]2-. [e]3-. [f]*talo*.

ment of the phenoxy substituent. Alternatively, the isolation of methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-allopyranoside (**6**) in yields of 4–28% (see Table I) suggested that formation of the 3-(phenylsulfate) (**3**) had occurred, followed by nucleophilic substitution at C-3 by the neighboring O-2 anion. In all of the reactions, some of the 2,3-di-(phenylsulfate) (**4**) was also obtained (see Table I).

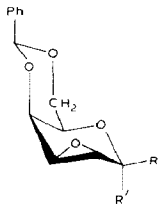
In comparable reactions of the β-glucoside (**8**), none of its 2-(phenylsulfate) (**9**) was obtained, although, understandably, the latter would have been an intermediate in the formation of methyl 2,3-anhydro-4,6-*O*-benzylidene-β-D-mannopyranoside (**12**) (29%, see Table II). The 3-(phenylsulfate) (**10**) would have served as a precursor to the 2,3-anhydro-β-alloside (**7**) (43%, see Table II). Some disubstitution to give **11** (13%) was also detected at −10°.

Little regioselectivity was observed (see Table II) in the reactions of methyl 4,6-*O*-benzylidene-α-D-galactopyranoside (**13**). Over the temperature range of −40 to +25°, the major product was the 2,3-di-(phenylsulfate) (**14**). Minor products isolated consisted of the 2-(phenylsulfate) (**15**) and 3-(phenylsulfate) (**16**). Also formed, in a yield of 17%, was methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-talopyranoside (**17**), attributable to an intramolecular displacement within **15**. Minor yields of the 2,3-cyclic sulfate (**19**) were obtained.

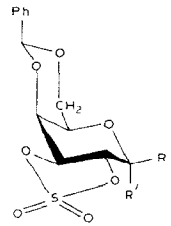
Anhydride formation was the principal outcome of the reaction of the β-D-galactopyranoside **21** at room temperature, as a 69% yield of methyl 2,3-anhydro-



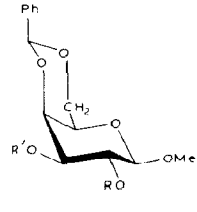
13 R = R′ = H
14 R = R′ = $PhOSO_2$
15 R = $PhOSO_2$, R′ = H
16 R = H, R′ = $PhOSO_2$



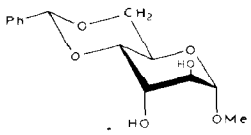
17 R = H, R′ = OMe
18 R = OMe, R′ = H



19 R = H, R′ = OMe
20 R = OMe, R′ = H



21 R = R′ = H
22 R = H, R′ = $PhOSO_2$
23 R = R′ = $PhOSO_2$



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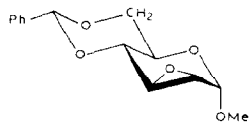

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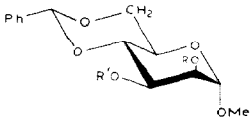
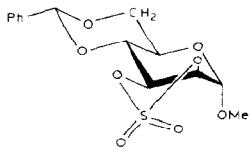


26 R = R′ = H
27 R = R′ = $PhOSO_2$



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4,6-*O*-benzylidene-β-D-talopyranoside (**18**) was obtained (see Table II). That the latter was derived through the intermediacy of the 3-(phenylsulfate) **22** was shown by the isolation of **22** in 71% yield when the reaction was conducted at −25°. By contrast, when the 3-(phenylsulfate) was treated with sodium hydride in oxolane, it afforded 57% of the 2,3-cyclic sulfate (**20**), plus **18** in a yield of 20%; yields of the 2,3-di-(phenylsulfate) **23** were minor.

No product containing sulfur was recovered from the reactions of methyl 4,6-*O*-benzylidene-α-D-altropyranoside (**24**) with phenyl chlorosulfate over the temperature range of −20 to +25° (see Table II). Intramolecular displacement was so readily facilitated that the products obtained were methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-mannopyranoside (**25**; 49–83%) and methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-allopyranoside (**6**; 4–13%). Evidence of regioselectivity was not apparent in the reaction of methyl 4,6-*O*-benzylidene-α-D-mannopyranoside (**26**), in that if afforded (see Table II) a 1:4 mixture of the 2,3-di-(phenylsulfate) (**27**; 10–19%) and the 2,3-cyclic sulfate (**28**; 74–82%). Clearly, the latter could have arisen from a 2- or a 3-(phenylsulfate) intermediate.

Overall, these reactions of phenyl chlorosulfate in the presence of sodium hydride furnish, in accord with earlier observations[5–7], several instances of relatively high regioselectivity for either O-2 or O-3 of 4,6-*O*-benzylidenealdohexopyranosides[5]. Of potential usefulness synthetically, for example, is the *α-gluco* 2-(phenylsulfate) (**2**), obtained in low-temperature reactions. In other respects, however, the reaction characteristics of the phenylsulfate group, under the conditions employed here, limit its applicability as a substituent. Hence, an appropriately positioned O-2 or O-3 anion of a mono-(phenylsulfate) derivative generated *in situ* may cause attack on either a nearby sulfur atom or a neighboring carbon atom, to yield a 2,3-cyclic sulfate* or a 2,3-oxirane, respectively.

The relative proportions of these secondary products are sometimes readily attributable to the stereochemistry encountered. For example, the high yield of cyclic sulfate **28** in the *manno* series, wherein O-2 and O-3 are *cis*, contrasts with the exclusive formation of epoxides in the *altro* series, which (in the ground state) contains trans-diaxially oriented O-2 and O-3. Neither pathway predominates in the *gluco* series, as both cyclic sulfate and epoxide formation are almost equally favored in the secondary, neighboring-group participation reactions. The facility with which a phenylsulfate substituent may be displaced, as evident from these findings, has also been demonstrated[4] in reactions involving the anomeric position.

A detailed account of the ^{1}H- and ^{13}C-n.m.r.-spectral characteristics of the 2,3-anhydro derivatives **6, 7, 12, 17, 18,** and **25**, and related compounds, has been presented[9].

Conformations of 2,3-cyclic sulfates. — The group of isomeric tricyclic com-

*It is also worth noting that the 2,3-cyclic sulfate substituent is itself susceptible to nucleophilic substitution, as illustrated[8] in the reaction of **28** with fluoride ion for the synthesis of a 2-deoxy-2-fluoro-D-glucose.

TABLE III

^1H–^1H COUPLING DATA (Hz) FOR 2,3-CYCLIC SULFATES AND RELATED MONO- AND DI-(PHENYLSULFATES) OF 4,6-*O*-BENZYLIDENEALDOHEXOPYRANOSIDES

Isomer	J	*Parent compound*	*2,3-Cyclic sulfate*	*2,3-Di-(phenyl-sulfate)*	*2-(Phenyl-sulfate)*	*3-(Phenyl-sulfate)*
α-gluco	1,2	3.9	3.1	3.7	3.8 (3.6)[a]	
	2,3	9.2	10.0	9.6	9.4 (9.4)[a]	
	3,4	9.2	9.7	9.5	9.5 (9.8)[a]	
α-manno	1,2	1.4	1.4	1.8		
	2,3	3.7	4.0	3.3		
	3,4	9.2	9.2	10.0		
α-galacto	1,2	3.6	3.2	3.2	3.6 (3.4)[a]	3.3 (3.4)[a]
	2,3	9.9	11.1	10.3	10.2 (10.5)[a]	10.3 (10.7)[a]
	3,4	3.5	3.0	3.0	3.3 (3.7)[a]	3.4 (3.5)
β-galacto	1,2	7.6	7.7	7.6		7.6 (8.0)[a]
	2,3	9.7	10.6	10.0		9.2 (10.3)[a]
	3,4	3.7	3.0	4.1		3.7 (3.8)[a]

[a]Spacings in parentheses are for the corresponding 2-*O*- or 3-*O*-acetyl derivative.

pounds described here includes both 2,3-*trans (gluco, galacto)* and 2,3-*cis (manno)*, 5-membered cyclic sulfates, as well as both *trans*-fused *(gluco, manno)* and *cis*-fused *(galacto)* 4,6-*O*-benzylidene substituents. According to the vicinal ^1H–^1H-coupling parameters found for these compounds, the closure of the cyclic sulfate rings appears to cause little, if any, distortion of the $^4C_1$ conformations of these aldopyranosides. This conclusion is based on the fact that the values of $J_{1,2}$, $J_{2,3}$, and $J_{3,4}$ (see Table III) are almost invariably of the magnitude expected; *e.g.*, the values of ~10 Hz for $J_{2,3}$ (*gluco, galacto* isomers) and for $J_{3,4}$ (*gluco, manno* isomers), and of 3–4 Hz for $J_{1,2}$ (*α-gluco, α-galacto* isomers) and for $J_{3,4}$ (*galacto* isomers). Comparative data for the corresponding 2,3-di-(phenylsulfates) and either the 2- or 3-(phenylsulfates), included in Table III, also reflect the same pyranoside chair conformations.

Also merited is a comparison of the shielding characteristics of a cyclic sulfate substituent with those of a phenyl sulfate. Deshielding of the α-hydrogen atom by the latter type of substituent averages ~1.5 p.p.m., as shown (see Table IV) by the chemical shifts of H-2 and H-3 of the 2,3-di-(phenylsulfates), or H-2 of the 2-phenylsulfates, relative to those of the non-substituted derivatives. This value is much larger than the downfield shifts of ~0.8 p.p.m. associated with a secondary, ionic, sulfate. In common with the latter, a phenylsulfate group on O-2 leads also to substantial deshielding of the adjacent anomeric proton, a characteristic that has served as a useful parameter in the n.m.r.-spectral analysis[10,11] of polysaccharide sulfates.

By contrast, the 2,3-cyclic sulfates exhibit a less uniform set of chemical-shift data. Because the pyranoside rings appear to maintain relatively unperturbed chair

TABLE IV

EFFECT OF 2,3-CYCLIC SULFATE AND PHENYLSULFATE SUBSTITUENTS ON THE ^1H CHEMICAL SHIFTS[a] OF METHYL 4,6-*O*-BENZYLIDENE-D-ALDOHEXOPYRANOSIDES

Isomer	*H atom*	*Parent compound (δ)*	*2,3-Cyclic sulfate*		*2,3-Di-(phenylsulfate)*	
			δ	Δδ	δ	Δδ
α-gluco	1	4.45	4.23	−0.18	5.05	0.60
	2	3.50	4.01	0.51	4.78	1.28
	3	3.81	5.03	1.22	5.53	1.72
	4	3.27	3.23	−0.04	3.14	−0.13
α-galacto	1	4.72	5.41	0.69	5.33	0.61
	2	3.90	5.26	1.36	5.30	1.40
	3	3.77	5.45	1.68	5.47	1.70
	4	3.68	4.86	1.08	4.44	0.76
β-galacto[b]	1	4.23	4.78	0.55	4.74	0.51
	2	4.03	5.24	1.21	5.42	1.39
	3	3.72	5.10	1.38	5.68	1.96
	4	3.92	4.22	0.30	4.60	0.68
α-manno	1	4.65	4.26	−0.39	5.06	0.41
	2	3.90	4.29	0.39	5.79	1.89
	3	3.99	4.30	0.31	5.48	1.49
	4	3.85	4.12	0.27	4.04	0.19

[a]δ; solvent, C_6D_6. [b]Solvent, 1:19 Me_2SO-d_6–C_6D_6.

forms, as already noted, this indicates that the variations observed are attributable mainly to the individual cyclic sulfate rings. For example, in comparing the 2,3-*trans*-fused compounds (see Table IV), the fact that H-2 and H-3 (as well as their H-1 and H-4 neighbors) of the *gluco* isomer are much more strongly shielded than those of the *galacto* isomers suggests that the two S=O bonds are more distant from the ring protons in the latter than in the former. In the *α-gluco* isomer, moreover, these S=O bonds appear (from molecular models) likely to be oriented more symmetrically with respect to axial H-1 and H-4 than in the *α-manno* isomer. This may account for the observation (see Table IV) that its H-1 and H-4 chemical shifts are affected about equally, relative to the non-substituted compound, whereas H-1 and H-4 of the *α-manno* isomer are, respectively, more shielded and less shielded, with an overall difference of 0.66 p.p.m.

EXPERIMENTAL

General methods. — Solutions were usually evaporated below 40° under diminished pressure. Melting points were determined with a Fisher–Johns apparatus, and are uncorrected. Elemental analyses were performed by Guelph Chemical Laboratories Ltd., Guelph, Ontario, Canada. Optical rotations were determined at r.t. for solutions in 1-dm tubes, with a JASCO DIP140 digital polarimeter. Oxolane (THF) was boiled under reflux with potassium and benzophenone under

nitrogen, and freshly distilled before use. The sodium hydride (50% dispersion) was washed with petroleum ether (b.p. 30–60°), and dried. Silica gel Merck (230–400 mesh ASTM) was used for flash column chromatography, and aluminum sheets of silica gel 60 F_{254} Merck were used for t.l.c. The solvent was benzene containing 2.5% (solvent *A*), 5% (*B*), or 10% (*C*) of ethyl acetate. Reaction bath temperatures of −25° and −40° were respectively obtained with carbon dioxide admixed with carbon tetrachloride and with acetonitrile. Phenyl chlorosulfate was freshly prepared, as previously described[3], and stored in the cold. I.r. spectra were recorded with a Perkin–Elmer 298 infrared spectrophotometer. Mass spectra were recorded at the Biomedical Mass Spectrometry Unit, McGill University. Nuclear magnetic resonance spectra were recorded with a Varian XL 200 or XL 300 instrument. Chemical shifts (δ) are reported with reference to tetramethylsilane, and coupling constants are reported in Hz.

General procedure for reactions of phenyl chlorosulfate with methyl 4,6-O-benzylidenealdohexopyranosides. — A mixture of sodium hydride (2 or 3 mmol) and oxolane (50 mL) was stirred under nitrogen, the sugar derivative (1.8 mmol) was introduced, stirring was continued for 1 h at the reaction temperature chosen, and the phenyl chlorosulfate (1 or 2 mol/mol of D-glucoside) was added under anhydrous conditions. At the end of the reaction period, the suspension was filtered, the filtrate evaporated, the residue extracted with dichloromethane, and the extracts combined, washed successively with water, 10% acetic acid, sodium hydrogencarbonate, and water, dried, and evaporated. The residue was subjected to column chromatography.

Methyl 4,6-O-benzylidene-α-D-glucopyranoside 2,3-di-(phenylsulfate) (**4**). — This was isolated from the reaction of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside[12] (**1**) by column chromatography (solvent *B*) as a white solid which was recrystallized from chloroform–hexane; m.p. 131–133° (dec.), $[\alpha]_D$ +27.5° (*c* 1.4, $CHCl_3$); $\lambda_{max}^{CHCl_3}$ 1415 (s) and 1200 (w) cm^{-1} (SO_2); ^{1}H-n.m.r. data (C_6D_6): δ 7.67–7.05 (m, 15 H, Ph), 5.53 (t, 1 H, $J_{3,4}$ 9.52 Hz, H-3), 5.23 (s, 1 H, PhC*H*), 5.05 (d, 1 H, $J_{1,2}$ 3.67 Hz, H-1), 4.78 (dd, 1 H, $J_{2,3}$ 9.61 Hz, H-2), 3.94 (dd, 1 H, $J_{6,6'}$ 10.22 Hz, H-6), 3.64 (m, 1 H, $J_{5,6}$ 4.75 Hz, H-5), 3.29 (t, 1 H, $J_{5,6'}$ 10.14 Hz, H-6'), 3.14 (t, 1 H, $J_{4,5}$ 9.78 Hz, H-4), and 2.72 (s, 3 H, O*CH*$_3$).

Anal. Calc. for $C_{26}H_{26}O_{12}S_2$: C, 52.52; H, 4.41; S, 10.79. Found: C, 52.75; H, 4.69; S, 10.52.

Methyl 4,6-O-benzylidene-α-D-glucopyranoside 2,3-cyclic sulfate (**5**). — Compound **5** was obtained by column chromatography (solvent *B*) as a white solid; m.p. 109–110° (dec.) after recrystallization from chloroform–hexane, $[\alpha]_D$ +69.7° (*c* 1.13, $CHCl_3$) (lit.[5] m.p. 103–106°, $[\alpha]_D$ +69°); $\lambda_{max}^{CHCl_3}$ 1400 (s) and 1200 (w) cm^{-1} (SO_2); ^{1}H-n.m.r. data (C_6D_6): δ 7.57–7.15 (m, 5 H, Ph), 5.15 (s, 1 H, PhC*H*), 5.03 (t, 1 H, $J_{3,4}$ 9.67 Hz, H-3), 4.23 (d, 1 H, $J_{1,2}$ 3.12 Hz, H-1), 4.01 (dd, 1 H, $J_{2,3}$ 10.04 Hz, H-2), 3.43 (dd, 1 H, $J_{5,6}$ 4.45 Hz, H-5), 3.85 (m, 1 H, $J_{6,6'}$ 9.86 Hz, H-6), 3.28 (dd, 1 H, $J_{5,6'}$ 2.53 Hz, H-6'), 3.23 (dd, 1 H, $J_{4,5}$ 10.16 Hz, H-4, overlapping with H-6'), and 2.72 (s, 3 H, O*CH*$_3$). Calc. for $C_{14}H_{16}O_8S$: mol. wt. 344. Found: *m/z* 345 (M + H).

Methyl 4,6-O-benzylidene-α-D-glucopyranoside 2-(phenylsulfate) (**2**) *and its O-acetyl derivative.* — Compound **2** was a white semisolid material obtained by column chromatography (solvent *B*); after recrystallization from ether–hexane, m.p. 110–112° (dec.), $[\alpha]_D$ +85.6° (*c* 1, $CHCl_3$); $\lambda_{max}^{CHCl_3}$ 3460–3410 (b, OH), 1405 (s), and 1200 (w) cm^{-1} (SO_2); ^{1}H-n.m.r. data (C_6D_6): δ 7.58–6.85 (m, 10 H, Ph), 5.21 (s, 1 H, PhC*H*), 5.06 (d, 1 H, $J_{1,2}$ 3.76 Hz, H-1), 4.66 (dd, 1 H, $J_{2,3}$ 9.43 Hz, H-2), 4.09 (dd, 1 H, $J_{3,4}$ 9.49 Hz, H-3), 4.01 (dd, $J_{5,6}$ 4.86 Hz, H-6), 3.71 (m, 1 H, $J_{5,6'}$ 10.17 Hz, H-5), 3.35 (t, 1 H, $J_{6,6'}$ 10.19 Hz, H-6), 3.07 (t, 1 H, $J_{4,5}$ 9.62 Hz, H-4), and 2.91 (s, 3 H, OCH_3).

Anal. Calc. for $C_{20}H_{22}O_9S$: C, 54.79; H, 5.06; S, 7.31. Found: C, 54.72; H, 5.12; S, 7.22.

Compound **2** was acetylated in ether–acetic anhydride containing 4-(dimethylamino)pyridine for 2 h at room temperature. The acetate was purified by chromatography on silica gel (solvent *A*), and crystallization from ether–hexane gave white needles; m.p. 92–93°, $[\alpha]_D$ +61.2° (*c* 1.2, $CHCl_3$); $\lambda_{max}^{CHCl_3}$ 1760 (s, O–C=O), 1400 (b), and 1200 (b) cm^{-1} (SO_2); ^{1}H-n.m.r. data (C_6D_6): δ 7.57–7.06 (m, 10 H, 2 Ph), 6.05 (t, 1 H, $J_{3,4}$ 9.81 Hz, H-3), 5.23 (s, 1 H, PhC*H*), 4.84 (d, 1 H, $J_{1,2}$ 3.62 Hz, H-1), 4.79 (dd, 1 H, $J_{2,3}$ 9.37 Hz, H-2), 3.98 (dd, 1 H, $J_{6,6'}$ 10.28 Hz, H-6), 3.77 (m, 1 H, $J_{5,6}$ 4.79 Hz, H-5), 3.35 (t, 1 H, $J_{5,6'}$ 10.19 Hz, H-6'), 3.25 (t, 1 H, $J_{4,5}$ 9.76 Hz, H-4), 2.79 (s, 3 H, OCH_3), and 1.64 (s, 3 H, CH_3–C=O). Calc. for $C_{22}H_{24}O_{10}S$: mol. wt. 480, Found. *m/z* 481 (M + H).

Methyl 2,3-anhydro-4,6-O-benzylidene-α-D-allopyranoside (**6**). — Isolated chromatographically (solvent *B*) from the reaction of α-glucoside **1**, the solid **6** was recrystallized from ether–hexane to give fine needles; m.p. 198–200°, $[\alpha]_D$ +140.9° (*c* 0.66, $CHCl_3$) (lit.[8,13] m.p. 199–200°, $[\alpha]_D$ 140.4°); ^{1}H-n.m.r. data (C_6D_6): δ 7.83–7.11 (m, 5 H, Ph), 5.31 (s, 1 H, PhC*H*), 4.36 (dd, 1 H, $J_{1,2}$ 2.87 Hz, H-1), 4.29 (m, 1 H, $J_{5,6}$ 5.07 Hz, H-5), 4.05 (m, 1 H, $J_{6,6'}$ 10.50 Hz, H-6), 3.44 (dd, 1 H, $J_{4,5}$ 9.1 Hz, H-4), 3.40 (t, 1 H, $J_{5,6'}$ 10.11 Hz, H-6), 3.12 (s, 3 H, OCH_3), 3.08 (bd, 1 H, $J_{3,4}$ 1.48 Hz, H-3), and 2.88 (dd, 1 H, $J_{2,3}$ 4.28 Hz, H-2). Calc. for $C_{14}H_{16}O_5$: mol. wt. 264. Found: *m/z* 265 (M + H).

Methyl 2,3-anhydro-4,6-O-benzylidene-β-D-allopyranoside (**7**). — Methyl 4,6-*O*-benzylidene-β-D-glucopyranoside[12] (**7**; 0.5 g, 1.8 mmol) was treated with phenyl chlorosulfate (0.5 mL, 3.6 mmol) in the presence of sodium hydride (0.25 g) for 48 h. Column chromatographic separation (solvent *B*) of the mixture of products afforded compound **7** (0.20 g, 43%); m.p. 138–139°, after crystallization from ether–hexane, $[\alpha]_D$ −15.5° (*c* 1.1, $CHCl_3$) (lit.[14] m.p. 138°, $[\alpha]_D$ −15.6°); ^{1}H-n.m.r. data (C_6D_6): δ 7.60–7.11 (m, 5 H, Ph), 5.26 (s, 1 H, PhC*H*), 4.56 (s, 1 H, $J_{1,2}$ 0.92 Hz, H-1), 4.08 (dd, 1 H, $J_{6,6'}$ 10.12 Hz, H-6), 3.77 (m, 1 H, $J_{5,6}$ 4.88 Hz, H-5), 3.60 (dd, 1 H, $J_{4,5}$ 9.90 Hz, H-4), 3.43 (t, 1 H, $J_{5,6'}$ 10.02 Hz, H-6), 3.16 (s, 3 H, OCH_3), 3.12 (bd, 1 H, $J_{3,4}$ 1.32 Hz, H-3), and 3.06 (dd, 1 H, $J_{2,3}$ 4.36 Hz, H-2). Calc. for $C_{14}H_{16}O_5$: mol. wt. 264. Found: *m/z* 265 (M + H).

Methyl 2,3-anhydro-4,6-O-benzylidene-β-D-mannopyranoside (**12**). — Also obtained by column chromatography (solvent *B*) from the reaction of **8** was **12** (135

mg, 29%); it was recrystallized from ether–hexane; m.p. 183–184°, $[\alpha]_D$ −31° (*c* 2.0, $CHCl_3$) (lit.[14] m.p. 183°, $[\alpha]_D$ −30.7°); ^{1}H-n.m.r. data (C_6D_6): δ 7.60–7.10 (m, 5 H, Ph), 5.13 (s, 1 H, PhC*H*), 4.33 (d, 1 H, $J_{1,2}$ 0.97 Hz, H-1), 4.02 (dd, 1 H, $J_{6,6'}$ 10.25 Hz, H-6), 3.54 (d, 1 H, $J_{4,5}$ 9.40 Hz, H-4), 3.44 (t, 1 H, $J_{5,6'}$ 10.20 Hz, H-6'), 3.29 (s, 3 H, OCH_3), 3.16 (d, 1 H, $J_{3,4}$ 0 Hz, H-3), 2.97 (m, 1 H, $J_{5,6}$ 4.64 Hz, H-5), and 2.71 (d, 1 H, $J_{2,3}$ 3.74 Hz, H-2). Calc. for $C_{14}H_{16}O_5$: mol. wt. 264. Found: *m/z* 265 (M + H).

*Methyl 4,6-O-benzylidene-β-*D*-glucopyranoside 2,3-di(phenylsulfate)* (**11**). — From the reaction of **8** at −10°, 0.14 g (13%) of compound **11** was isolated by column chromatography (solvent *B*); m.p. 122–123° after crystallization from chloroform–ether, $[\alpha]_D$ −33.4° (*c* 0.5, $CHCl_3$); $\lambda_{max}^{CHCl_3}$ 1415 (s) and 1195 (w) cm^{-1} (SO_2); ^{1}H-n.m.r. data (1:9 Me_2SO-d_6–C_6D_6): δ 7.60–6.90 (m, 15 H, 3 Ph), 5.72 (t, 1 H, $J_{3,4}$ 9.03 Hz, H-3), 5.42 (s, 1 H, PhC*H*), 5.12 (dd, 1 H, $J_{2,3}$ 9.09 Hz, H-2), 4.82 (d, 1 H, $J_{1,2}$ 7.77 Hz, H-1), 4.15 (dd, 1 H, $J_{6,6'}$ 9.58 Hz, H-6), 3.78 (t, 1 H, $J_{4,5}$ 8.71 Hz, H-4), 3.69 (m, 1 H, $J_{5,6}$ 4.3 Hz, H-5), 3.59 (t, 1 H, $J_{5,6'}$ 10.01 Hz, H-6'), and 3.24 (s, 3 H, OCH_3).

Anal. Calc. for $C_{26}H_{26}O_{12}S_2$: C, 52.52; H, 4.41; S, 10.79. Found: C, 52.14; H, 4.51; S, 10.95.

*Methyl 2,3-anhydro-4,6-O-benzylidene-α-*D*-mannopyranoside* (**25**). — Isolated, together with **6**, by column chromatography (solvent *B*) from the reaction of methyl 4,6-*O*-benzylidene-α-D-altropyranoside[15] (**24**) at room temperature, compound **25** had m.p. 148–150° after recrystallization from ether, $[\alpha]_D$ +107.2° (*c* 1, $CHCl_3$) (lit.[13] m.p. 147°, $[\alpha]_D$ +107.4°); ^{1}H-n.m.r. data (C_6D_6): δ 7.57–7.13 (m, 5 H, Ph), 5.20 (s, 1 H, PhC*H*), 4.61 (s, 1 H, $J_{1,2}$ 0.62 Hz, H-1), 4.04 (m, 1 H, $J_{6,6'}$ 10.26 Hz, H-6), 3.72 (m, 1 H, $J_{5,6}$ 4.49 Hz, H-5), 3.56 (d, 1 H, $J_{4,5}$ 9.47 Hz, H-4), 3.42 (t, 1 H, $J_{5,6'}$ 10.25 Hz, H-6'), 3.25 (d, 1 H, $J_{3,4}$ 0 Hz, H-3), 3.12 (s, 3 H, OCH_3), and 2.86 (d, 1 H, $J_{2,3}$ 3.60 Hz, H-2). Calc. for $C_{14}H_{16}O_5$: mol. wt. 264. Found: *m/z* 265 (M + H).

*Methyl 4,6-O-benzylidene-α-*D*-mannopyranoside 2,3-di-(phenylsulfate)* (**27**). — Formed in the reaction of methyl 4,6-*O*-benzylidene-α-D-mannopyranoside[16] (**26**) at either −25° or room temperature, and isolated by column chromatography (solvent *B*), the solid was recrystallized from chloroform–ether; m.p. 133–134°, $[\alpha]_D$ −91.1° (*c* 1.1, $CHCl_3$); ^{1}H-n.m.r. data (C_6D_6): δ 7.51–7.13 (m, 15 H, 3 Ph), 5.79 (dd, 1 H, $J_{2,3}$ 3.25 Hz, H-2), 5.48 (dd, 1 H, $J_{3,4}$ 9.97 Hz, H-3), 5.06 (d, 1 H, $J_{1,2}$ 1.84 Hz, H-1), 5.05 (s, 1 H, PhC*H*), 4.04 (t, 1 H, $J_{4,5}$ 9.65 Hz, H-4), 3.97 (dd, 1 H, $J_{6,6'}$ 10.15 Hz, H-6), 3.64 (m, 1 H, $J_{5,6}$ 4.71 Hz, H-5), 3.40 (t, 1 H, $J_{5,6'}$ 10.10 Hz, H-6'), and 2.72 (s, 3 H, OCH_3).

Anal. Calc. for $C_{26}H_{26}O_{12}S_2$: C, 52.52; H, 4.41; S, 10.79. Found: C, 52.45; H, 4.47; S, 10.76.

*Methyl 4,6-O-benzylidene-α-*D*-mannopyranoside 2,3-cyclic sulfate* (**28**). — The solid **28** isolated by column chromatography (solvent *B*) was recrystallized from ether–hexane; m.p. 104–105° (lit.[8] m.p. 98°), $[\alpha]_D$ −50.8° (*c* 1.1, $CHCl_3$); $\lambda_{max}^{CHCl_3}$ 1400 (s), 1195 (w), 1180 (m), 1145 (s), and 980 (s) cm^{-1}; ^{1}H-n.m.r. data

(C_6D_6): δ 7.46–7.14 (m, 5 H, Ph), 5.05 (s, 1 H, PhC*H*), 4.30 (dd, 1 H, $J_{3,4}$ 9.23 Hz, H-3), 4.29 (dd, 1 H, $J_{2,3}$ 4.02 Hz, H-2), 4.26 (b, 1 H, $J_{1,2}$ 1.39 Hz, H-1), 4.12 (m, 1 H, $J_{4,5}$ 8.97 Hz, H-4), 3.89 (dd, 1 H, $J_{6,6'}$ 10.22 Hz, H-6), 3.38 (m, 1 H, $J_{5,6}$ 4.82 Hz, H-5), 3.27 (t, 1 H, $J_{5,6'}$ 9.86 Hz, H-6'), and 2.65 (s, 3 H, OCH_3). Calc. for $C_{14}H_{16}O_8S$: mol. wt. 344. Found: *m/z* 345 (M + H).

*Methyl 4,6-O-benzylidene-α-*D*-galactopyranoside 2,3-di-(phenylsulfate)* (**14**). — Isolated by column chromatogaphy (solvent *C*) from reactions of the α-galactoside[17] **13** in yields of 39, 52, and 73% at −40, −20°, and room temperature, the white solid was recrystallized from chloroform–ether to give **14**; m.p. 148.9°, $[\alpha]_D$ +126.1° (*c* 1.4, $CHCl_3$); $\lambda_{max}^{CHCl_3}$ 1415 (s) and 1200 (w) cm^{-1} (SO_2); ^{1}H-n.m.r. data (C_6D_6): δ 7.70–6.70 (m, 15 H, 3 Ph), 5.47 (dd, 1 H, $J_{3,4}$ 3.0 Hz, H-3), 5.33 (d, 1 H, $J_{1,2}$ 3.12 Hz, H-1), 5.30 (dd, 1 H, $J_{2,3}$ 10.34 Hz, H-2), 5.17 (s, 1 H, PhC*H*), 4.44 (dd, 1 H, $J_{4,5}$ 1.18 Hz, H-4), 3.86 (dd, 1 H, $J_{6,6'}$ 12.65 Hz, H-6), 3.10 (dd, 1 H, $J_{5,6'}$ 1.77 Hz, H-6'), 2.91 (s, 3 H, OCH_3), and 2.79 (br, 1 H, $J_{5,6}$ 1.64 Hz, H-5).

Anal. Calc. for $C_{26}H_{26}O_{12}S_2$: C, 52.52; H, 4.41; S, 10.79; Found: C, 52.55; H, 4.63; S, 10.96.

*Methyl 4,6-O-benzylidene-α-*D*-galactopyranoside 2,3-cyclic sulfate* (**19**). — Compound **19** was isolated by column chromatography (solvent *C*) in yields of 15 and 8% at room temperature and −20°, respectively. The solid isolated was recrystallized from a large volume of chloroform and a few drops of ether, to give very fine crystals; m.p. 130–132° (dec.), $[\alpha]_D$ +147.3° (*c* 1.1, C_5H_5N); ^{1}H-n.m.r. data (Me_2SO): δ 7.70–7.48 (m, 5 H, Ph), 5.75 (s, 1 H, PhC*H*), 5.45 (dd, 1 H, $J_{3,4}$ 2.96 Hz, H-3), 5.41 (d, 1 H, $J_{1,2}$ 3.2 Hz, H-1), 5.26 (d, 1 H, $J_{2,3}$ 11.1 Hz, H-2), 4.86 (d, 1 H, $J_{4,5}$ 0.5 Hz, H-4), 4.15 (m, 2 H, H-6,6'), 3.86 (d, 1 H, $J_{5,6}$ 1.52 Hz, H-5), and 3.47 (s, 3 H, OCH_3).

Anal. Calc. for $C_{14}H_{16}O_8S$: C, 48.83; H, 4.68; S, 9.31. Found: C, 48.65; H, 5.01; S, 9.25.

*Methyl 4,6-O-benzylidene-α-*D*-galactopyranoside 2-(phenylsulfate)* (**15**) *and its 3-acetate*. — Compound **15** was isolated by column chromatography (solvent *C*) from the reaction of **13** at −40 and −20° in yields of 18 and 19%, respectively, and recrystallized from chloroform–ether; m.p. 110.2° (dec.), $[\alpha]_D$ +113.0° (*c* 1.1, $CHCl_3$); $\lambda_{max}^{CHCl_3}$ 1400 (b) and 1220 (w) cm^{-1} (SO_2); ^{1}H-n.m.r. data (1:19 Me_2SO-d_6–C_6H_6): δ 7.70–7.00 (m, 10 H, 2 Ph), 5.40 (s, 1 H, PhC*H*), 5.33 (dd, 1 H, $J_{2,3}$ 10.16 Hz, H-2), 5.26 (d, 1 H, $J_{1,2}$ 3.56 Hz, H-1), 4.35 (dd, 1 H, $J_{3,4}$ 3.31 Hz, H-3), 4.05 (d, 1 H, $J_{4,5}$ 1.15 Hz, H-4), 4.00 (dd, 1 H, $J_{6,6'}$ 12.24 Hz, H-6), 3.56 (dd, 1 H, $J_{5,6'}$ 2.02 Hz, H-6'), 3.19 (b, 1 H, $J_{5,6}$ 1.6 Hz, H-5), and 3.05 (s, 3 H, OCH_3).

Anal. Calc. for $C_{20}H_{22}O_9S$: C, 54.79; H, 5.06: S, 7.31. Found: C, 54.81; H, 4.98; S, 7.32.

The 3-*O*-acetyl derivative, prepared quantitatively as described for the acetate of **2**, was recrystallized from ether–hexane; m.p. 107–108° (dec.), $[\alpha]_D$ 159.6° (*c* 1.1, $CHCl_3$); ^{1}H-n.m.r. data (1:19 Me_2SO-d_6–C_6D_6): δ 7.57–6.89 (m, 10 H, 2 Ph), 5.65 (dd, 1 H, $J_{3,4}$ 3.7 Hz, H-3), 5.48 (dd, 1 H, $J_{2,3}$ 10.45 Hz, H-2), 5.31 (s, 1 H, PhC*H*), 5.13 (d, 1 H, $J_{1,2}$ 3.39 Hz, H-1), 4.28 (dd, 1 H, $J_{4,5}$ 1.64 Hz, H-4),

3.95 (dd, 1 H, $J_{6,6'}$ 12.40 Hz, H-6'), 3.52 (dd, 1 H, $J_{5,6'}$ 1.75 Hz, H-6'), 3.17 (d, 1 H, $J_{5,6}$ 1.81 Hz, H-5), 3.01 (s, 3 H, OCH_3), and 1.65 (s, 3 H, CH_3–C=O). Calc. for $C_{22}H_{24}O_{10}S$: mol. wt. 480. Found: *m/z* 481 (M + H).

Methyl 4,6-O-benzylidene-α-D-galactopyranoside 3-(phenylsulfate) (**16**) *and its 2-acetate.* — Obtained from the reaction of **13** at −40 and −20° in yields of 8 and 17%, respectively, and isolated by column chromatography (solvent *C*), compound **16** was recrystallized from chloroform–ether; m.p. 117–120°, $[\alpha]_D$ +156.4° (*c* 1.3, $CHCl_3$); ^{1}H-n.m.r. data (1:19 Me_2SO-d_6–C_6D_6): δ 7.56–6.86 (m, 10 H, 2 Ph), 5.38 (dd, 1 H, $J_{3,4}$ 3.39 Hz, H-3), 5.31 (s, 1 H, PhC*H*), 4.90 (d, 1 H, $J_{1,2}$ 3.3 Hz, H-1), 4.52 (dd, 1 H, $J_{4,5}$ 1.36 Hz, H-4), 4.51 (m, 1 H, $J_{2,3}$ 10.25 Hz, H-2), 3.98 (dd, 1 H, $J_{6,6'}$ 12.45 Hz, H-6); 3.51 (dd, 1 H, $J_{5,6'}$ 1.62 Hz, H-6'), and 3.15 (s, 4 H, H-5 and OCH_3, overlapping).

Anal. Calc. for $C_{20}H_{22}O_9S$: C, 54.79; H, 5.06; S, 7.31. Found: C, 54.86; H, 5.25; S, 6.96.

The 2-*O*-acetyl derivative of **16** was prepared, and was recrystallized from ether–hexane, m.p. 127–128° (dec.), $[\alpha]_D$ +140° (*c* 1.1, $CHCl_3$); ^{1}H-n.m.r. data (1:19 Me_2SO-d_6–C_6D_6): δ 7.57–6.85 (m, 10 H, 2 Ph), 5.67 (dd, 1 H, $J_{2,3}$ 10.66 Hz, H-2), 5.46 (dd, 1 H, $J_{3,4}$ 3.53 Hz, H-3), 5.30 (s, 1 H, PhC*H*), 5.09 (d, 1 H, $J_{1,2}$ 3.4 Hz, H-1), 4.37 (dd, 1 H, $J_{4,5}$ 1.13 Hz, H-4), 3.97 (dd, 1 H, $J_{6,6'}$ 12.43 Hz, H-6), 3.52 (dd, 1 H, $J_{5,6'}$ 2.01 Hz, H-6'), 3.05 (b, 1 H, $J_{5,6}$ 1.3 Hz, H-5), 3.01 (s, 3 H, OCH_3), and 1.64 (s, 3 H, CH_3–C=O). Calc. for $C_{22}H_{24}O_{10}S$: mol. wt. 480. Found: *m/z* 481 (M + H).

Methyl 2,3-anhydro-4,6-O-benzylidene-α-D-talopyranoside (**17**). — Isolated by column chromatography (solvent *C*) from the reaction of **13** at room temperature, only (30 mg, 6%). Recrystallized from chloroform–ether, it had m.p. 239–240°, $[\alpha]_D$ −25° (*c* 0.65, $CHCl_3$) (lit.[18] m.p. 242°, $[\alpha]_D$ −40°); ^{1}H-n.m.r. data (1:19 Me_2SO-d_6–C_6D_6): δ 7.50–7.10 (m, 5 H, Ph), 5.37 (s, 1 H, PhC*H*), 4.83 (s, 1 H, $J_{1,2}$ ~0 Hz, H-1), 4.01 (dd, 1 H, $J_{6,6'}$ 12.75 Hz, H-6), 3.81 (dd, 1 H, $J_{4,5}$ 2.62 Hz, H-4), 3.71 (s, 1 H, $J_{5,6'}$ ~0 Hz, H-6'), 3.21 (m, 1 H, $J_{5,6}$ 2.79 Hz, H-5), 3.20 (dd, 1 H, $J_{3,4}$ 5.64 Hz, H-3), 3.12 (s, 3 H, OCH_3), and 2.87 (d, 1 H, $J_{2,3}$ 3.63 Hz, H-2).

Methyl 4,6-O-benzylidene-β-D-galactopyranoside 2,3-di-(phenylsulfate) (**23**). — Compound **23** (40 mg, 4%) was isolated by column chromatography (solvent *C*) from a reaction at −25° in which a 1:1 molar equivalence of β-galactoside **21** and phenyl chlorosulfate was used. It crystallized from ether to give fine crystals; m.p. 133–135°, $[\alpha]_D$ +15.6° (*c* 1.35, $CHCl_3$); ^{1}H-n.m.r. data (1:19 Me_2SO-d_6–C_6D_6): δ 7.42–6.83 (m, 15 H, 3 Ph), 5.68 (dd, 1 H, $J_{3,4}$ 4.07 Hz, H-3), 5.42 (dd, 1 H, $J_{2,3}$ 10.01 Hz, H-2), 5.24 (s, 1 H, PhC*H*), 4.74 (dd, 1 H, $J_{1,2}$ 7.59 Hz, H-1), 4.60 (d, 1 H, $J_{4,5}$ 1.29 Hz, H-4), 4.02 (dd, 1 H, $J_{6,6'}$ 12.76 Hz, H-6), 3.55 (dd, 1 H, $J_{5,6'}$ 2.12 Hz, H-6'), 3.42 (b, 1 H, $J_{5,6}$ 2.05 Hz, H-5), and 3.31 (s, 3 H, OCH_3).

Anal. Calc. for $C_{26}H_{26}O_{12}S_2$: C, 52.52; H, 4.41; S, 10.79. Found: C, 52.37; H, 4.40; S, 11.09.

Methyl 4,6-O-benzylidene-β-D-galactopyranoside 3-(phenylsulfate) (**22**) *and its 2-acetate.* — Compound **22** was isolated by column chromatography (solvent *C*),

yields of 26 and 71% of **22** were obtained when one and two equivalents, respectively, of phenyl chlorosulfate reacted at −25° with **21**. Crystallized from $CHCl_3$, it had m.p. 113–115°, $[\alpha]_D$ +38.6° (*c* 1.19, $CHCl_3$); ^{1}H-n.m.r. data (1:19 Me_2SO-d_6–C_6D_6): δ 7.56–6.14 (m, 10 H, 2 Ph), 5.09 (dd, 1 H, $J_{3,4}$ 3.72 Hz, H-3), 5.31 (s, 1 H, PhC*H*), 4.44 (d, 1 H, $J_{4,5}$ 1.15 Hz, H-4), 4.34 (d, 1 H, $J_{1,2}$ 7.64 Hz, H-1), 4.26 (dd, 1 H, $J_{2,3}$ 9.19 Hz, H-2), 4.04 (dd, 1 H, $J_{6,6'}$ 12.25 Hz, H-6), 3.51 (dd, 1 H, $J_{5,6'}$ 1.59 Hz, H-6'), 3.45 (s, 3 H, OCH_3), and 2.92 (m, 1 H, $J_{5,6}$ 1.59 Hz, H-5).

Anal. Calc. for $C_{20}H_{22}O_9S$: C, 54.79; H, 5.06; S, 7.31. Found: C, 55.15; H, 5.24; S, 7.20.

The 2-*O*-acetyl derivative of **22** crystallized from chloroform–ether; m.p. 128–130°, $[\alpha]_D$ +29.5° (*c* 1.1, $CHCl_3$); ^{1}H-n.m.r. data (1:19 Me_2SO-d_6–C_6D_6): δ 7.27–7.08 (m, 10 H, 2 Ph), 5.82 (dd, 1 H, $J_{2,3}$ 10.31 Hz, H-2), 5.25 (s, 1 H, PhC*H*), 5.24 (dd, 1 H, $J_{3,4}$ 3.80 Hz, H-3), 4.44 (d, 1 H, $J_{1,2}$ 7.99 Hz, H-1), 4.29 (dd, 1 H, $J_{4,5}$ 1.10 Hz, H-4), 4.03 (dd, 1 H, $J_{6,6'}$ 12.51 Hz, H-6), 3.53 (dd, 1 H, $J_{5,6'}$ 1.65 Hz, H-6'), 3.31 (s, 3 H, OCH_3), 3.10 (b, 1 H, $J_{5,6}$ 1.77 Hz, H-5), and 1.75 (s, 3 H, CH_3–C=O). Calc. for $C_{22}H_{24}O_{10}S$: mol. wt. 480. Found: *m/z* 481 (M + H).

*Methyl 2,3-anhydro-4,6-O-benzylidene-β-*D*-talopyranoside* (**18**). Compound **18** was obtained in a yield of 69% from the reaction of β-galactoside **21** with 2 equivalents of phenyl chlorosulfate at room temperature. The white solid material isolated by column chromatography (solvent *C*) had m.p. 245–248, after recrystallization from chloroform–ether, $[\alpha]_D$ −141.3° (*c* 0.9, pyridine) (lit.[19] m.p. 246°, $[\alpha]_D$ −142.5°); ^{1}H-n.m.r. data (C_6D_6): δ 7.40–7.10 (m, 5 H, Ph), 5.29 (s, 1 H, PhC*H*), 4.24 (s, 1 H, $J_{1,2}$ ~0 Hz, H-1), 4.03 (dd, 1 H, $J_{5,6}$ 1.2 Hz, H-6), 3.45 (dd, 1 H, $J_{6,6'}$ 12.50 Hz, H-6'), 3.42 (s, 3 H, OCH_3), 3.33 (dd, 1 H, $J_{4,5}$ 2.74 Hz, H-4), 2.90 (dd, 1 H, $J_{3,4}$ 4.86 Hz, H-3), 2.73 (d, 1 H, $J_{2,3}$ 4.10 Hz, H-2), and 2.27 (m, 1 H, $J_{5,6'}$ 3.04 Hz, H-5).

*Methyl 4,6-O-benzylidene-β-*D*-galactopyranoside 2,3-cyclic sulfate* (**20**). — Obtained as the major product (57% yield) by treatment of methyl 4,6-*O*-benzylidene-β-D-galactopyranoside 3-(phenylsulfate) (**22**) with 4 equivalents of NaH in oxolane for 4 h at room temperature, compound **20** was a solid material, isolated by column chromatography (solvent *C*), that was recrystallized from MeOH; it had m.p. 125–128°, $[\alpha]_D$ +11.2° (*c* 8.5, C_5H_5N); ^{1}H-n.m.r. data ($CDCl_3$): δ 7.48–7.25 (m, 5 H, Ph), 5.60 (s, 1 H, PhC*H*); 5.05 (dd, 1 H, $J_{2,3}$ 10.50 Hz, H-2), 4.97 (d, 1 H, $J_{1,2}$ 7.72 Hz, H-1), 4.69 (dd, 1 H, $J_{3,4}$ 2.96 Hz, H-3), 4.60 (dd, 1 H, $J_{4,5}$ 1.18 Hz, H-4), 4.40 (dd, 1 H, $J_{6,6}$ 12.83 Hz, H-6), 4.15 (dd, 1 H, $J_{5,6'}$ 1.39 Hz, H-6'), 3.63 (b, 1 H, $J_{5,6}$ 1.83 Hz, H-5), and 3.59 (s, 3 H, OCH_3).

Anal. Calc. for $C_{14}H_{16}O_8S$: C, 48.83; H, 4.68; S, 9.31. Found: C, 48.69; H, 4.86; S, 9.35.

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REFERENCES

1 J. R. TURVEY, *Adv. Carbohydr. Chem.*, 20 (1963) 183–218.
2 K. TAKIURA AND S. HONDA, *Yakugaku Zasshi*, 87 (1967) 1248–1255.
3 C. L. PENNEY AND A. S. PERLIN, *Carbohydr. Res.*, 93 (1981) 241–246.
4 M. M. ABDEL-MALIK AND A. S. PERLIN, *Carbohydr. Res.*, 189 (1989) 123–133.
5 H. J. JENNINGS AND J. K. N. JONES, *Can. J. Chem.*, 41 (1963) 1151–1159.
6 J. K. N. JONES, M. B. PERRY, AND J. C. TURNER, *Can. J. Chem.*, 38 (1960) 1122–1129.
7 H. J. JENNINGS AND J. K. N. JONES, *Can. J. Chem.*, 43 (1965) 2372–2386.
8 T. J. TEWSON, *J. Org. Chem.*, 48 (1983) 3507–3510.
9 M. M. ABDEL-MALIK, Q.-J. PENG, AND A. S. PERLIN, *Carbohydr. Res.*, 159 (1987) 11–23.
10 W. M. PASIKA AND L. H. CRAGG, *Can. J. Chem.*, 41 (1963) 777–781.
11 A. S. PERLIN, M. MAZUREK, L. B. JAQUES, AND L. W. KAVANAGH, *Carbohydr. Res.*, 7 (1968) 369–379.
12 D. M. HALL, *Carbohydr. Res.*, 86 (1980) 158–160.
13 G. J. ROBERTSON AND C. F. GRIFFITH, *J. Chem. Soc.*, (1935) 1193–1201.
14 W. H. MEYERS AND G. J. ROBERTSON, *J. Am. Chem. Soc.*, 65 (1943) 8–11.
15 N. K. RICHTMYER AND C. S. HUDSON, *J. Am. Chem. Soc.*, 63 (1941) 1727–1731.
16 J. G. BUCHANAN AND J. C. P. SCHWARZ, *J. Chem. Soc.*, (1962) 4770–4777.
17 G. J. ROBERTSON AND R. A. LAMB, *J. Chem. Soc.*, (1934) 1321–1322.
18 E. SORKIN AND T. REICHSTEIN, *Helv. Chim. Acta*, 28 (1945) 1–12.
19 J. W. H. OLDHAM AND D. J. BELL, *J. Am. Chem. Soc.*, 60 (1938) 323–325.