Conversion of One Hydroxy Group in a Diol to a Phenyl Ether with Triphenylbismuth Diacetate, a New Glycol Reaction Showing Strong Axial Preference in Six-Membered Rings

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After being refluxed for a few hours, a dichloromethane solution of a diol with triphenylbismuth diacetate gave in most cases excellent yields of a monophenyl ether. No diphenylated products were found. Tertiary hydroxy groups were only phenylated in bis tertiary diols, and then in poor yield. Increasing the distance between the hydroxy groups up to six carbon atoms decreased the speed of the reaction which nevertheless was still preparatively useful. Diols in flexible rings behaved like their acyclic counterparts. The course of the reaction was also examined with some conformationally rigid molecules: *trans*-4-*tert*-butyl-*cis*-2-hydroxycyclohexanol, *trans*-4-*tert*-butyl-*trans*-2-hydroxycyclohexanol, cholestane-2α,3α-diol, cholestane-2α,3β-diol, and pyranoside derivatives with the α-D-gluco, α-D-manno, α-D-galacto, and α-D-allo configurations. The phenylations of *cis*-diols were strongly regioselective for axial epimers, while those of trans, bis equatorial diols were undiscriminate and often much slower. A feasible general mechanism is proposed to explain these results.

In a recent preliminary paper,[1] we described a new reaction of diols with triphenylbismuth diacetate, which resulted in the phenylation of one hydroxy group of the diol. We now report these experiments in full, together with an extension to alicyclic and steroid diols and to carbohydrate derivatives. Triphenylbismuth diacetate is one out of a family of several pentavalent bismuth reagents found most useful by Barton et al. for the selective oxidation of alcohols to aldehydes or ketones,[2] glycol cleavage,[2,3] and α-phenylation of carbonyl derivatives.[4] These authors reported that triphenylbismuth diacetate was less convenient in this respect than other bismuth(V) derivatives such as triphenylbismuth carbonate; nevertheless, we selected it in a systematic study of the reactions of stannylenes with glycol cleavage reagents, because of its solubility in orgaic solvents.[5] Stannylenes underwent cleavage with triphenylbismuth diacetate, but, unexpectedly, the parent glycols were converted to monophenyl ethers in good yield.

This reaction, which appears to be general, is interesting in three respects: (a) the conditions are very mild, (b) the phenyl etherification of one alcoholic function is possible only if there is another one, suitably located, in the same molecule, (c) the reagent shows a strong preference for the phenylation of axial hydroxy groups in six-membered rings.

Although this reaction is possible only with diols, it is interesting to compare it with the few methods available for the direct phenylation of isolated hydroxy groups since it is well-known that the nucleophilic substitution of unactivated aryl halides is unpracticable under the usual conditions. Thus, the reaction of potassium *tert*-butoxide with bromobenzene in dimethyl sulfoxide solution[6] and the phenylations of simple alcoholates with diphenyliodonium[7] or diphenylbromonium[8] salts involve strongly alkaline conditions and a great excess of alcohol. Phenylation with diazonium salts appears milder, but again the alcohol is used in excess, as the solvent. Consequently, none of these methods would be suitable for the phenylation of costly alcohols. On the other hand, our new reaction utilizes stoichiometric amounts of reagents in boiling dichloromethane, and the conditions are weakly acidic.

Results and Discussion

Phenylation of Aliphatic and Flexible Alicyclic Diols. Approach to a General Mechanism. Tables I and II give the results of experiments with these simple models. Refluxing for a few hours a dichloromethane solution containing equimolecular quantities of a glycol and triphenylbismuth diacetate gave in most cases very good yields of phenoxy alcohols. These were isolated by silica gel column chromatography of the reaction mixture, and their homogeneity was checked by VPC. Solid ethers were crystallized to a constant melting point. The structures were easily ascertained by mass spectrometry. In most cases, an intense peak corresponding to phenol was found, besides a molecular ion of variable intensity. Another fragmentation, that is

$$CR^1R^2(OPh)CR^3R^4OH \rightarrow R^1R^2COPh + R^3R^4COH$$

appeared likely since such fragments should be stabilized by the oxygen atom. Peaks corresponding to the mass of R^1R^2COPh were generally evident on the spectra of the phenyl ethers of vicinal aliphatic glycols **16–25**. Such peaks would be superimposed onto the molecular peak when arising from alicyclic derivatives (Table II). As expected, this bond rupture is not favored when the carbon atoms are not both oxygenated, and peaks with the mass of $PhOCH_2$ are very weak on the spectra of nonvicinal phenoxy alcohols **27–31** (Table I).

Ambiguities in the location of the phenoxy group were solved by proton NMR spectroscopy. The multiplicity of the signals for labile hydroxy protons indicated the nature, primary, secondary or tertiary, of the alcohol in compounds **21–24** (Table I) and **38–41** (Table II). This inference was checked by the examination of the signal of the proton(s) geminal to OH, which was simplified, or at least made thinner by the addition of deuterium oxide, while the signal of the proton(s) geminal to OPh remained unalterated by this treatment. This is how the assignments given in the Experimental Section were elicited, and it can be verified in each case that the alternative structure would be incompatible with the spectrum. As a rule, in sym-

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Table I. Reaction of Aliphatic and Phenyl-Substituted Aliphatic Glycols with Triphenylbismuth Diacetate[a]

glycol	phenyl ether	isolated yield, %
CH_2OHCH_2OH (1)	CH_2OPhCH_2OH (16)	85
(±)-$CH_3CHOHCHOHCH_3$ (2)	$CH_3CHOPhCHOHCH_3$ (17)	86
meso-$CH_3(CH_2)_2CHOHCHOH(CH_2)_2CH_3$ (3)	*meso*-$CH_3(CH_2)_2CHOPhCHOH(CH_2)_2CH_3$ (18)	91
meso-PhCHOHCHPhOH (4)	PhCHOPhCHPhOH (19)	37
$(CH_3)_2C(OH)C(CH_3)_2OH$ (5)[b]	$(CH_3)_2COPhC(CH_3)_2OH$ (20)	15
$Ph_2C(OH)CPh_2OH$ (6)[b]		0
$CH_3CHOHCH_2OH$ (7)	$CH_3CHOHCH_2OPh$ (21), $CH_3CHOPhCH_2OH$ (22)	92[c]
PhCHOHCH$_2$OH (8)	PhCHOHCH$_2$OPh (23)	43
	PhCHOPhCH$_2$OH (24)	48
$(CH_3)_2COHCHOHCH_3$ (9)	$CH_3CHOPhC(CH_3)_2OH$ (25)	84
$CH_3PhCOHCHOHPh$ (10)	$PhCHOPhC(CH_3)PhOH$ (26)[d]	50
$CH_2OHCH_2CH_2OH$ (11)	$CH_2OPhCH_2CH_2OH$ (27)	87
$CH_2OH(CH_2)_2CH_2OH$ (12)	$CH_2OPh(CH_2)_2CH_2OH$ (28)	80
$CH_2OH(CH_2)_3CH_2OH$ (13)	$CH_2OPh(CH_2)_3CH_2OH$ (29)	50
$CH_2OH(CH_2)_4CH_2OH$ (14)	$CH_2OPh(CH_2)_4CH_2OH$ (30)	40
(*Z*)-$CH_2(OH)CH=CHCH_2OH$ (15)	(*Z*)-$CH_2OPhCH=CHCH_2OH$ (31)	75

[a] Reaction time 4–5 h. [b] Exceptionally the reaction time was 24 h. [c] Combined yield of mixed phenyl ethers. [d] Glycol splitting (also observed with 4 and 6) could be repressed to 26% by the addition of one equivalent of acetic acid to the mixture.

Table II. Reaction of Relatively Flexible Alicyclic Glycols with Triphenylbismuth Diacetate[a]

glycol	phenyl ether	isolated yield, %
cis-cyclopentane-1,2-diol (32)[b]	*cis*-2-phenoxycyclopentanol (38)	41
trans-cyclopentane-1,2-diol (33)	*trans*-2-phenoxycyclopentanol (39)	51
cis-cyclohexane-1,2-diol (34)	*cis*-2-phenoxycyclohexanol (40)	87
trans-cyclohexane-1,2-diol (35)	*trans*-2-phenoxycyclohexanol (41)	88
trans-1-methylcyclohexane-1,2-diol (36)	*trans*-1-methyl-2-phenoxycyclohexanol (42)	88
trans-1-phenylcyclohexane-1,2-diol (37)	*trans*-2-phenoxy-1-phenylcyclohexanol (43)	74

[a] Reaction time, 4 h. [b] Exceptionally, the mixture was refluxed for 7 h.

Table III. Reaction of Conformationally Rigid Cyclohexanediols with Triphenylbismuth Diacetate

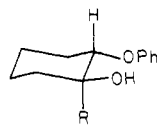
glycol	reaction time, h	isolated yield, % axial phenoxy	isolated yield, % equatorial phenoxy	isolated yield, % equatorial phenoxy
trans-4-*tert*-butyl-*cis*-2-hydroxycyclohexanol (44)	7	73	2	
trans-4-*tert*-butyl-*trans*-2-hydroxycyclohexanol (47)	16		44	44
cholestane-2α,3α-diol (50)	7	60		
cholestane-2α,3β-diol (52)	60		5	5

metrical diols, the signal of the proton geminal to OPh was observed 0.1–0.4 ppm downfield from that of the proton geminal to OH.

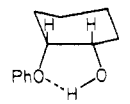
In the spectra of the alicyclic ethers **42** and **43** (Chart I), the ^3J coupling constants of protons CH–OPh, which lie in the vicinity of 4 and 11 Hz, are best interpreted by a chair conformation with an equatorial phenoxy group and an axial methyl or phenyl. On the other hand, in ether **40**, the signal of the CH–O protons are both pseudotriplets, with J = 3, 3, and 7.5 Hz so that the depicted half-chair conformation **40**, which avoids an axial substituent and allows for hydrogen bonding, is probably the preferred one.

This smooth phenylation of an alcoholic hydroxy group will occur only if another one is present in the same molecule: refluxing for 24 h a mixture of cyclohexanol and triphenylbismuth diacetate in dichloromethane solution gave at most 3% phenoxycyclohexane, while the conversion of cyclohexane-1,2-diol with the same reagent was practically complete within 4 h. Although some etherification of octan-1-ol could be observed under forcing conditions, no reaction could be detected under conditions which generated monophenyl ethers of diols in more than 60% yield. Compounds with at least one hydroxy group, expected to be sensitive to electrophiles, such as **52** (Table III) or **55** (Table IV) react very sluggishly, because their structure is not otherwise adquate, a proof that the reaction does not involve a single OH. Finally, there was no evidence for the presence of bis phenyl ethers among the reaction products from the many diols investigated in this

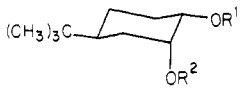
Chart I



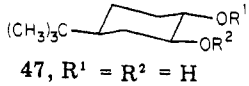
42, R = CH_3
43, R = Ph



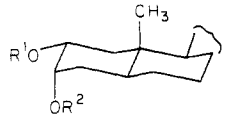
40



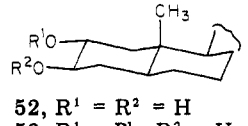
44, $R^1 = R^2 = H$
45, R^1 = Ph; R^2 = H
46, R^1 = H; R^2 = Ph



47, $R^1 = R^2 = H$
48, R^1 = Ph; R^2 = H
49, R^1 = H; R^2 = Ph



50, $R^1 = R^2 = H$
51, R^1 = H; R^2 = Ph



52, $R^1 = R^2 = H$
53, R^1 = Ph; R^2 = H
54, R^1 = H; R^2 = Ph

Table IV. Reaction of Partially Protected Pyranosides with Triphenylbismuth Diacetate

pyranoside	yield of phenyl ether %		
	axial	equatorial	primary
benzyl 2,3-di-*O*-benzyl-α-D-glucopyranoside (**55**)		13	15
methyl 4,6-*O*-benzylidene-α-D-glucopyranoside (**58**)		traces	
benzyl 4,6-*O*-benzylidene-α-D-mannopyranoside (**59**)	42	11	
benzyl 6-*O*-trityl-α-D-mannopyranoside (**62**)		32[a]	
benzyl 2,3-di-*O*-benzyl-β-D-galactopyranoside (**64**)	26		11
benzyl 2,6-di-*O*-benzyl-α-D-galactopyranoside (**67**)	30	4	
methyl 2-*O*-allyl-6-*O*-trityl-α-D-allopyranoside (**70**)	27	3	
methyl 4,6-*O*-benzylidene-α-D-allopyranoside (**73**)	0	0	

[a] This was the 3-*O*-phenyl ether. The mixture of 2- and 4-*O*-phenyl ethers was isolated in 23% yield.

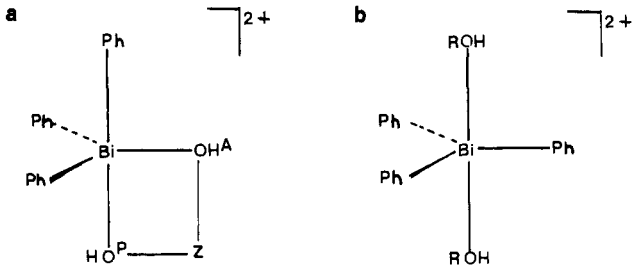


Figure 1. Suggested intermediates in the reactions of triphenylbismuth diacetate (a) with diols and (b) with monoalcohols.

work. In a series of bis primary alkanediols with increasing chain length (1 and 11–14, Table I) the yields were practically the same for 1,2-, 1,3-, and 1,4-diols and under identical reaction times lessened only for 1,5- and 1,6-diols. However, this effect of the distance between the hydroxy groups was not dramatic. The yield was good with the more rigid 1,4-diol **15** (Table I).

The above experiments point out that the phenylation of one oxygen, the acceptor A, involves another hydroxy group, the participant P. It appears that the participation function is less exacting in steric requirements than the acceptor function. A secondary OH on cyclohexane practically does not react when alone but is smoothly phenylated when next to a tertiary OH (see **36** and **37**; Table II). Thus the tertiary OH may be a good participant, as also in the case of diols **9** and **10** (Table I). But then, the unreactivity of the ditertiary glycols **5** and **6** indicates that the tertiary hydroxy group is a poor phenyl acceptor. Thus we conclude that the receptor site for the participating hydroxy group P is less sterically demanding than the receptor site for the phenyl acceptor A.

Such a disparity exists between the apical and equatorial positions in a trigonal bipyramid, which is the usual conformation of five-ccordinate triphenylated bismuth(V) complexes. This led us to postulate a chelated intermediate, with the disposition of ligands shown in Figure 1a. This model appears to account satisfactorily for all the peculiarities of the reaction found so far.

Known five-coordinate triphenylated bismuth(V) complexes comply with the general rule that electronegative ligands are apical in the most stable conformations.[9-14] But the bis apical chelation of a vicinal glycol is impossible for steric reasons, and the next best choice should be apical–equatorial chelation. This conformation has one further advantage: the bismuthadioxacyclopentane ring would be almost free of angular strain at the bismuth atom. The reason for this is that in such a ring, owing to the length of the Bi–O bond (2.1 Å or more), normal angles at the carbon and oxygen atoms involve a Bi–O–Bi angle near 80°, not far from 90°. Finally, we expect the oxygen O^P of the participant hydroxy group to lie in the apical position, for presumably this mode of bonding should be less sensitive to steric hinderance, because of the greater length of apical bonds. [These may be as long as 2.63 Å in the bridged complex $(Ph_3BiOClO_3)_2O$ with probable high ionic character.[12,13]] Thus the acceptor oxygen atom is equatorial.

We suggest that the driving force for the decomposition of this intermediate to the phenyl ether is the tendency of the apical phenyl group to escape from its unfavorable position by migrating onto the nearby equatorial oxygen atom. The loss of the hydroxy proton may be a prerequisite to this transformation. Similar reductive eliminations have been observed with compounds Ph_3BiX_2 (X = F, Cl, Br),[15] but they only occur at higher temperatures, probably because the phenyl groups occupy the presumably more stable equatorial positions in these molecules in their ground state and show little tendency to eliminate. This observation being kept in mind, the specificity of the reaction for diol systems is readily understood. If two hydroxy groups belong to different molecules, nothing prevents them from coordinating both at apical positions, giving a more stable arrangement with equatorial phenyl groups (Figure 1b). Then, reductive elimination will only occur under forcing conditions. This mechanism also explains why the yield of the reaction with the longer chain diols **12–14** does not decrease so very quickly. The chains of moderate length cannot chelate the two apical positions by passing round the phenyl groups, which prevents the building of this synthetically inefficient configuration.

Axial Preference in the Phenylation of Conformationally Rigid Cyclohexanediols (Table III). We assume chair conformations wtih an equatorial *tert*-butyl substituent for cyclohexane derivatives **44–49** or as depicted for the A ring of the cholestanediols **50–54**.

The hydroxy groups of the starting compounds are axial at C-2 in diol **44** and at C-3 in cholestane-2α,3α-diol (**50**). In all other cases they are equatorial. Structure assignments for the phenylation products rest on the values of vicinal coupling constants, measured after removal of labile hydroxy protons, a large vicinal coupling (8–12 Hz) indicating axial conformation for a proton.

Phenylation of diol **44** practically gave only one ether, **46**, in very good yield (Table III). The equatorial orientation of the free hydroxy group in **46** was proved by the

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(14) Beaumont, R. E.; Goel, R. G.; Prasad, H. S. *Inorg. Chem.* **1973**, *12*, 944.
(15) Challenger, F.; Wilkinson, J. F. *J. Chem. Soc.* **1922**, *121*, 91.

large, 10.5 Hz, axial–axial coupling of the geminal proton at δ 3.64. Thus, the phenylated oxygen was the axial one, and, as a confirmation, a narrow signal (8 Hz at half height) was found at δ 4.53 for the CH–OPh proton which was weakly coupled to three neighbors. Identical considerations led to structure 51, with an axial phenoxy group at C-3, for the major product of the phenylation of cholestane-2α,3α-diol, which was obtained in good yield. The spectra of **46** and **51** were almost superimposable below 2.5 ppm. Structure **51** was confirmed by acetylation, which brought about a 1.2-ppm downfield shift of the proton with a large coupling.

The byproduct in this last reaction was perhaps the equatorial phenyl ether, but as it was not separated in the pure state, its constitution could not be safely determined.

On the other hand, the diequatorial *trans*-diol **47** gave in 88% total yield a 1:1 mixture of the isomeric phenyl ethers **48** and **49**. Their NMR spectra were almost identical but for the presence of a quadruplet (δ 1.40, J = 3, 12 Hz) separated from the bulk of ring protons in the spectrum of the less polar isomer. For both compounds, the protons geminal to oxygen appeared as first-order octuplets, near δ 3.70 and 4.00, with coupling constants in the vicinity of 4, 8, and 11 Hz.

The two ethers obtained in low yield in the inefficient phenylation of the diequatorial cholestane-2α,3β-diol **52** could not be separated from each other. In the NMR sectrum of the mixture, four octuplets of equal intensity (^3J near 4, 9, and 11 Hz) at 3.72, 3.90, 3.96, and 4.20 ppm were the expected signals of the axial 2-H and 3-H protons.

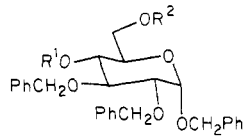
These experiments with vicinal glycols in conformationally biased or rigid six-membered rings (Table III) disclosed another property of the reagent: a strong preference for the phenylation of axial hydroxy groups. Thus equatorial–axial *cis*-diols gave axial phenoxy ethers in good yield, with excellent regioselectivity. On the other hand, diequatorial *trans*-diols reacted more slowly to give 1:1 mixtures of the two possible equatorial phenoxy derivatives. The overall yield from diol **47** was good.

The origin of this preference is not clear. Up to now, a certain number of reactions are known, which occur more rapidly with axial hydroxy groups or their derivatives than with the equatorial epimers.[16] The following are the oxidations of alcohols with chromium trioxide,[17] and (in one case[18])with μ-oxo-bis(chlorotriphenylbismuth): the solvolyses of tosylates,[19] the dissolving-metal reductions of acetates,[20] and the *N*-bromosuccinimide oxidations of alcohols.[21] In the chromium trioxide oxidations, epimeric alcohols give the same ketone, and the transition states could have comparable energies if they are productlike. This would favor the less stable axial epimer.[22-26] The differences of speed in solvolyses were interpreted in the same way, the common "product" now being the carbenium ion. The preferential reductions of axial acetates were explained[20] by the release of steric hinderance when the axial C–OAc bond is broken. The mechanism of the *N*-bromosuccinimide oxidations in the steroid field does not appear to have been studied any more since these were reported.

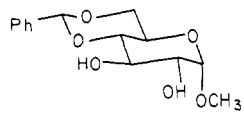
Obviously, none of these mechanisms can explain the preferential etherification of axial epimers by triphenylbismuth diacetate. Between this reaction and those above quoted, there are at least four major, obvious differences: (a) the geminal proton is not concerned, (b) the carbon–oxygen bond is not broken, (c) the carbon is still sp^3 hybridized in the product, and (d) the steric compression is higher, or in any case not much smaller in the product than in the starting alcohol. Actually, the common manifestation of axial preference in such different reactions suggests investigating a single comprehensive explanation.

Carbohydrate Derivatives (Table IV). Next we examined the phenylation of a number of partially protected pyranosides with two free hydroxy groups. These and their derivatives, i.e., compounds **55–73** (Chart II) are drawn in the D-$^4C_1$ conformation, which is known to be the most stable one for glucosides, galactosides, mannosides, and allosides.[27] The vicinal coupling constants were found to be consistent with this conformation, even in rings with the presumably bulky phenoxy groups in the axial position. Yields were generally lower in the phenylation of pyranosides, not exceeding 42% in the most favorable case. Still these reactions may be preparatively useful, especially as no other such simple method is available to prepare

Chart II



55, $R^1 = R^2 = H$
56, $R^1 = Ph$; $R^2 = H$
57, $R^1 = H$; $R^2 = Ph$



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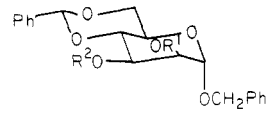
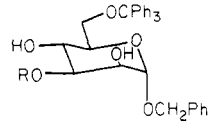
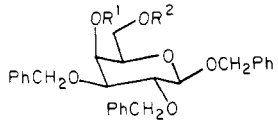


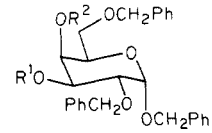
59, $R^1 = R^2 = H$
60, $R^1 = Ph$; $R^2 = H$
61, $R^1 = H$; $R^2 = Ph$



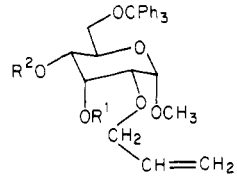
62, R = H
63, R = Ph



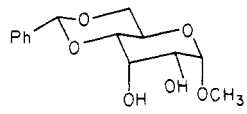
64, $R^1 = R^2 = H$
65, $R^1 = Ph$; $R^2 = H$
66, $R^1 = H$; $R^2 = Ph$



67, $R^1 = R^2 = H$
68, $R^1 = Ph$; $R^2 = H$
69, $R^1 = H$; $R^2 = Ph$



70, $R^1 = R^2 = H$
71, $R^1 = Ph$; $R^2 = H$
72, $R^1 = H$; $R^2 = Ph$



73

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carbohydrate phenyl ethers. We shall first discuss vicinal glycols. Methyl 4,6-*O*-benzylidene-α-D-glucopyranoside (**58**), selected as a representative diequatorial diol, was almost unaffected by the reagent. Benzyl 4,6-*O*-benzylidene-α-D-mannopyranoside (**59**) has one axial and one equatorial hydroxy group, at C-2 and C-3. The axial proton 3-H is strongly coupled to 4-H, while the equatorial proton 2-H shows only weak couplings. Reaction of the mannoside **59** with triphenylbismuth diacetate gave a mixture of phenyl ethers. Acetylation of the major one shifted the characteristic quadruplet of 3-H (^3J = 3.5 and 10 Hz) 1.2 ppm downfield in the NMR spectrum, thus proving structure **60**, with a phenoxy group on C-2 for the parent alcohol. Conversely, acetylation of the minor product shifted the quadruplet of 2-H (^3J = 1.5 and 3.5 Hz) 1.2 ppm downfield, a confirmation that the parent alcohol was structure **61** phenylated on 3-O.

Methyl 4,6-*O*-benzylidene-α-D-allopyranoside (**73**), which shows the alternative conformation of cis hydroxy groups at C-2 and C-3 in a D-pyranoside, was found unreactive. Maybe steric hinderance had become excessive. Derivatives with cis hydroxy groups at C-3 and C-4 were next examined. Benzyl 2,6-di-*O*-benzyl-α-D-galactopyranoside (**67**) gave two phenyl ethers in an 8:1 ratio. Acetylation of the major, less polar one shifted the characteristic quadruplet of the axial 3-H proton, (^3J = 3.5 and 10 Hz) 1.5 ppm downfield in the NMR spectrum. Thus the parent alcohol was the isomer phenylated on 4-O, **69**. The same kind of argument confirmed that the isomer isolated in very small yield was the 3-*O*-phenyl ether **68**, the shifted signal then being the narrow doublet of the equatorial proton 4-H (^3J = 3.5 Hz).

The allo derivative, methyl 2-*O*-allyl-6-*O*-trityl-α-D-allopyranoside (**70**) shows the alternative configuration of cis hydroxy groups on C-3 and C-4, so that now 3-H is equatorial (^3J = 3 and 3 Hz) and 4-H axial (^3J = 3 and 10 Hz). Again the free hydroxy groups after phenylation were located by inspection of the NMR spectrum after acetylation, and structures **71** (axial phenoxy group) and **72** (equatorial phenoxy group) were respectively assigned to the major and minor phenyl ether.

The above experiments again indicate preferential phenylation of axial hydroxy groups in pyranose rings, that is, the same regioselectivity as with conformationally rigid cyclohexane derivatives.

Next we investigated two primary–secondary 1,3-diols, the benzyl 2,3-*O*-benzyl-hexopyranosides with the α-D-gluco (**55**) and β-D-galacto (**64**) configurations. Both gave a mixture of isomeric phenyl ethers. It seemed probable that the more polar derivatives were the 4-*O*-phenyl ethers with a primary alcoholic function **56** and **65**. This was confirmed by a comparison of the chemical shifts of 4-H, 6-H and 6′-H. In the more polar ethers, protons 4-H were found 0.5 ppm downfield and protons 6-H and 6′-H ca. 0.5 ppm upfield from their respective location in the spectra of the less polar ones. Thus the slightly more abundant isomer in the gluco series was the primary ether **57**, while the major isomer in the galacto series was the secondary, axial one, **65**. This result is interesting because the pyranosides **55** and **64** are both 1,3-primary–secondary diols, with identical configurations and conformations in the vicinity of the diol, except that the secondary hydroxy group is equatorial in the first one and axial in the second. We see (Table IV) that primary and equatorial OHs have comparable reactivities, while the axial OH is 2.5 times more reactive than the primary OH.

Finally, a triol with one axial hydroxy group was examined, as one aim of carbohydrate chemistry is to dispense with protecting groups. The result with benzyl 6-*O*-trityl-α-D-mannopyranoside (**62**) was unexpected. Chromatography separated one major isomer from a mixture of two minor products. Inspection of the NMR spectrum of the main product after acetylation showed that the signals of two protons had been shifted to the lower field side of the signal of 1-H. They were superimposed, and irradiation at their common frequency converted one quadruplet, at δ 4.68, to a singlet, therefore eliminating two couplings at the same time. The only compatible structure is that of a 2,4-di-*O*-acetylmannoside. Thus, in the parent diol, the phenoxy group was equatorial and on C-3 (structure **63**) rather than axial and on C-2.

Experimental Section

The reactions were monitored by TLC on Merck silica gel plates. Chromatographic separations were performed on silica gel columns, with CH_2Cl_2 as the eluent, unless otherwise specified. Gas–liquid chromatographic (GLC) analyses of reaction products were accomplished on an SE-30 column operating at the recorded temperature by using a Girdel instrument equipped with a flame-ionization detector. Melting points were taken with a Büchi capillary melting point apparatus and are uncorrected. The IR spectra were recorded on a Pye Unicam spectrophotometer. The ^1H NMR spectra were obtained with a Cameca 250-MHz spectrometer, with $CDCl_3$ as the solvent, unless otherwise specified. Chemical shifts (δ) are expressed in parts per million relative to internal tetramethylsilane. Spectra are generally not fully reported but were always found to be completely consistent with the given structures. Mass spectra were obtained from a Ribermag R 10-10 gas chromatograph–mass spectrometer and are reported as *m/e* (relative intensity, interpretation). Dichloromethane was rectified and stored over molecular sieves.

The following diols were synthesized according to literature methods: *trans*-4-*tert*-butyl-*cis*-2-hydroxycyclohexanol (**44**),[28] *trans*-4-*tert*-butyl-*trans*-2-hydroxycyclohexanol (**45**),[28] cholestane-2α,3α-diol (**50**),[29] cholestane-2α,3β-diol (**52**),[30] benzyl 2,3-di-*O*-benzyl-α-D-glucopyranoside (**55**),[31] benzyl 4,6-*O*-benzylidene-α-D-mannopyranoside (**59**),[32] benzyl 6-*O*-trityl-α-D-mannopyranoside (**62**),[33] benzyl 2,3-di-*O*-benzyl-α-D-galactopyranoside (**64**),[34] benzyl 2,6-di-*O*-benzyl-α-D-galactopyranoside (**67**),[35] methyl 4,6-*O*-benzylidene-α-D-allopyranoside (**73**).[36] Methyl 2-*O*-allyl-α-D-allopyranoside was a gift of Dr. J. M. Vatèle, from this Laboratory.

General Method. A solution of the diol (1 mmol) and triphenylbismuth diacetate (1 mmol) in dichloromethane (5 mL) was refluxed until TLC indicated no more transformation and then evaporated to dryness. The phenyl ether was separated from the residue by chromatography. The homogeneity of the sample was checked by GLC.

2-Phenoxyethanol (16): liquid; 85%; GLC at 160 °C; IR 3400 cm^{-1} (OH); ^1H NMR δ 2.92 (1 H, OH), 3.90 (2 H, 1-CH_2), 4.00 (2 H, 2-CH_2), 6.80–7.33 (5 H, Ph); mass spectrum, *m/e* (relative intensity) 138 (100, M^+), 94 (91, PhOH). Anal. Calcd for $C_8H_{10}O_2$: C, 69.54; H, 7.30. Found: C, 69.29; H, 7.42.

3-Phenoxybutan-2-ol (17): liquid; 86%; GLC at 160 °C; IR 3450 cm^{-1} (OH); ^1H NMR δ 1.24 (d, 3 H, CH_3), 1.26 (d, 3 H, CH_3), 2.71 (m, 1 H, OH), 3.82 (m, 1 H, 2-H), 4.12 (m, 1 H, 3-H), 6.80–7.34 (m, 5 H, Ph); mass spectrum, (relative intensity) *m/e* 166 (19, M^+), 94 (100, PhOH). Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H,

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8.49. Found: C, 72.12; H, 8.66.

(±)-5-Phenoxyoctan-4-ol (18): liquid; 91%; GLC at 190 °C; IR 3450 cm^{-1} (OH); ^1H NMR δ 2.00 (d, 1 H, J = 5 Hz, OH), 3.85 (m, 1 H, 4-H), 4.24 (m, 1 H, 5-H), 6.84–7.32 (m, 5 H, Ph); mass spectrum, m/e (relative intensity) 222 (37, M^+), 149 (43, C_3H_7CHOPh-), 94 (88, PhOH), 55 (100, C_4H_7·). Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.48; H, 10.03.

2-Phenoxy-1,2-diphenylethan-1-ol (19). Chromatography first gave benzaldehyde and then the phenyl ether **19**: liquid; 37%; GLC at 220 °C; IR 3450, 3550 cm^{-1} (OH); ^1H NMR δ 2.40 (1 H, OH), 5.00 (1 H, 1-H), 5.20 (d, 1 H, $J_{1,2}$ = 5 Hz, 2-H), 6.68–7.40 (15 H, Ph); mass spectrum, m/e (relative intensity) 290 (0.4, M^+), 183 (100, PhCHOPh), 94 (8, PhOH). Anal. Calcd for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25. Found: C, 82.47; H, 6.40.

2,3-Dimethyl-3-phenoxybutan-2-ol (20): liquid. 15%; GLC at 190 °C; IR 3450, 3560 cm^{-1} (OH); ^1H NMR δ 1.26 (s, 6 H, 2 CH_3's), 1.34 (s, 6 H, 2 CH_3's), 2.77 (s, 1 H, OH), 6.84–7.36 (5 H, Ph); mass spectrum, m/e (relative intensity) 194 (1.4, M^+), 135 (92, $(CH_3)_2COPh$), 94 (100, PhOH), 59 (27, $(CH_3)_2COH$). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.14; H, 9.45.

Mixture of 1-Phenoxypropan-2-ol (21) and 2-Phenoxypropan-1-ol (22): liquid; 92%; GLC at 160 °C; IR 3450 cm^{-1} (OH); ^1H NMR δ 1.18 (d, 3 H, J = 6 Hz, CH_3), 1.24 (d, 3 H, J = 6 Hz, CH_3), 3.10 (t, 1 H, CH_2OH), 3.22 (1 H, CHOH), 3.64 (q, 2 H, J = 4, 5 Hz, CH_2OH), 3.77 (octet, 2 H, J = 2, 3.5, 9 Hz, CH_2OPh), 4.09 (1 H, m, CHOH), 4.35 (m, 1 H, CHOPh), 6.78–7.30 (m, 5 H, Ph); mass spectrum, m/e (relative intensity) 152 (26, M^+), 94 (100, PhOH). Anal. Calcd for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 70.04; H, 7.80.

2-Phenoxy-1-phenylethan-1-ol (23). This was the less polar ether from the phenylation of **8**: crystals; 41%; mp 58 °C (petroleum ether); GLC at 220 °C; IR 3400 (OH), 1600, 1500 cm^{-1} (Ph); ^1H NMR δ 2.95 (d, 1 H, J = 3 Hz, OH), 4.05 (m, 2 H, CH_2), 5.10 (octet, 1 H, J = 3, 4.3, 7 Hz, CH), 6.80–7.50 (10 H, Ph); mass spectrum, m/e (relative intensity) 214 (20, M^+), 108 (100, $PhOCH_2$), 94 (41, PhOH). Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.60; H, 6.63.

2-Phenoxy-2-phenylethan-1-ol (24). This was the more polar ether in the phenylation of **8**: crystals; 43%; mp 81 °C (petroleum ether); GLC at 220 °C; IR 1500, 1600 (Ph), 3450 cm^{-1} (OH); ^1H NMR δ 2.53 (q, 1 H, J = 5.5, 7 Hz, OH), 3.90 (m, 2 H, CH_2), 5.27 (q, 1 H, J = 5, 7 Hz, CH), 6.80–7.50 (m, 10 H, Ph); mass spectrum m/e (relative intensity) 214 (1.8, M^+), 94 (100, PhOH). Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.57; H, 6.64.

2-Methyl-3-phenoxybutan-2-ol (25): liquid; 84%; GLC at 180 °C; IR 1500, 1600 (Ph), 3450 cm^{-1} (OH); ^1H NMR δ 1.24 (d, 3 H, J = 6 Hz, CH_3), 1.30 (s, 6 H, $C(CH_3)_2$), 2.40 (s, 1 H, OH), 4.18 (q, 1 H, CH), 6.86–7.34 (5 H, Ph); mass spectrum, m/e (relative intensity) 180 (17, M^+), 122 (57, $PhOCHCH_3H^+$), 121 (17, $PhOCHCH_3$), 94 (82, Ph), 59 (100, $(CH_3)_2COH$). Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.40; H, 9.09.

1-Phenoxy-1,2-diphenylpropan-2-ol (26). This was prepared by the general method except that acetic acid (60 mg) was added. Chromatography (hexane–ethyl acetate, 95:5) first separated benzaldehyde and acetophenone (26.5%) and then ether **26**: liquid; 50%; GLC at 220 °C; IR 1500, 1600 (Ph), 3400 cm^{-1} (OH); ^1H NMR δ 1.70 (s, 3 H, CH_3), 2.50 (s, 1 H, OH), 5.12 (s, 1 H, CH), 6.65–7.30 (15 H, Ph); mass spectrum, m/e (relative intensity) 304 (2, M^+), 184 (46, $PhCHOPhH^+$), 183 (26, PhCHOPh), 121 (71, $PhC(CH_3)OH$), 94 (3.5, PhOH). Anal. Calcd for $C_{21}H_{20}O_2$: C, 82.86; H, 6.62. Found: C, 82.95; H, 6.54.

3-Phenoxypropan-1-ol (27): liquid; 87%; GLC at 160 °C; IR 1500, 1600 (Ph), 3400 cm^{-1} (OH); ^1H NMR δ 2.00 (2 H, CCH_2C), 2.22 (1 H, OH), 3.80 (2 H, CH_2OH), 4.09 (2 H, CH_2OPh), 6.83–7.32 (5 H, Ph); mass spectrum m/e (relative intensity) 152 (64, M^+), 94 (100, PhOH). Anal. Calcd for $C_9H_{12}O_6$: C, 71.02; H, 7.95. Found: C, 70.86; H, 8.10.

4-Phenoxybutan-1-ol (28): liquid; 80%; GLC at 190 °C; IR 1500, 1600 (Ph), 3400 cm^{-1} (OH); ^1H NMR δ 1.63–1.94 (4 H, 2 CH_2), 2.20 (1 H, OH), 3.68 (t, 2 H, J = 6 Hz, 1-CH_2), 3.97 (t, 2 H, J = 6 Hz, 4-OH_2), 6.78–7.34 (5 H, Ph); mass spectrum, m/e (relative intensity) 166 (31, M^+), 94 (98, PhOH). Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 71.99; H, 8.62.

5-Phenoxypentan-1-ol (29): liquid; 50%; GLC at 190 °C; IR 1500, 1600 (Ph), 3400 cm^{-1} (OH); ^1H NMR δ 1.43–1.90 (7 H, 3 CH_2, OH), 3.68 (t, 2 H, J = 6 Hz, 1-CH_2), 3.95 (t, 2 H, J = 6 Hz, 5-CH_2), 6.84–7.30 (5 H, Ph); mass spectrum, m/e (relative intensity) 180 (31, M^+), 94 (100, PhOH). Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.08; H, 9.16.

6-Phenoxyhexan-1-ol (30): liquid; 41%; GLC at 220 °C; IR 1500, 1600 (Ph), 3400 cm^{-1} (OH); ^1H NMR δ 1.32–1.84 (8 H, 4 CH_2), 1.88 (1 H, OH), 3.61 (t, 2 H, J = 6 Hz, 1-CH_2), 3.92 (t, 2 H, J = 6 Hz, 6-CH_2), 6.80–7.30 (5 H, Ph); mass spectrum, m/e (relative intensity) 194 (34, M^+), 94 (100, PhOH). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.19; H, 9.44.

***(Z)*-4-Phenoxybut-2-en-1-ol (31)**: liquid; 75%; GLC at 190 °C; IR 1500, 1600 (Ph), 3400 cm^{-1} (OH); ^1H NMR δ 2.86 (1 H, OH), 4.22 (d, 2 H, J = 4.5 Hz, 1-CH_2), 4.57 (d, 2 H, J = 5 Hz, 4-CH_2), 5.80 (m, 2 H, CH=CH), 6.80–7.32 (5 H, Ph); mass spectrum, m/e (relative intensity) 164 (14, M^+), 94 (100, PhOH). Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37. Found: C, 72.86; H, 7.62.

***cis*-2-Phenoxycyclopentan-1-ol (38)**: liquid; 41%; GLC at 190 °C; IR 1500, 1600 (Ph), 3450 cm^{-1} (OH); ^1H NMR δ 1.20–2.14 (6 H, 3 CH_2), 2.44 (d, 1 H, J = 5.5 Hz, OH), 4.24 (pst, 1 H, J = 4.5, 5.5 Hz, 1 H), 4.53 (octet, 1 H, J = 1, 4.5, 9 Hz, 2-H), 6.86–7.33 (5 H, Ph); mass spectrum, m/e (relative intensity) 178 (13, M^+), 94 (100, PhOH). Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.14; H, 7.92. Found: C, 73.92; H, 8.04.

***trans*-2-Phenoxycyclopentan-1-ol (39)**: liquid; 50.5%; GLC at 190 °C; IR 1500, 1580, 1600 (Ph), 3400 cm^{-1} (OH); ^1H NMR δ 1.40–2.24 (6 H, 3 CH_2), 2.56 (s, 1 H, OH), 4.25 (br, 1 H, 1-H), 4.45 (dd, 1 H, J = 3, 6 Hz, 2-H), 6.74–7.27 (5 H, Ph); mass spectrum, m/e (relative intensity) 178 (45, M^+), 94 (100, PhOH). Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.07; H, 8.09.

***cis*-2-Phenoxycyclohexan-1-ol (40)**: liquid; 87%; GLC at 180 °C; IR 1500, 1600 (Ph), 3550 cm^{-1} (OH); ^1H NMR δ 1.00–2.00 (8 H, 4 CH_2), 2.28 (s, 1 H, OH), 3.93 (m, 1 H, 1-H), 4.36 (octet, 1 H, J = 3, 3, 8 Hz, 2-H), 6.80–7.30 (5 H, Ph); mass spectrum, m/e (relative intensity) 192 (64, M^+), 94 (100, Ph). Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.16; H, 8.30.

***trans*-2-Phenoxycyclohexan-1-ol (41)**: crystals; 88%; mp 82 °C (ether–petroleum ether) (lit.[37] mp 81–82 °C); IR 1500, 1600 (Ph), 3450 cm^{-1} (OH). Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 75.21; H, 8.45.

***trans*-1-Methyl-2-phenoxycyclohexan-1-ol (42)**: liquid; 88%; GLC at 190 °C; IR 1500, 1600 (Ph), 3450 cm^{-1} (OH); ^1H NMR δ 1.35–2.00 (8 H, 4 CH_2), 2.34 (s, 1 H, OH), 4.09 (dd, 1 H, J = 3.5, 9 Hz, 2-H), 6.92–7.26 (5 H, Ph); mass spectrum, m/e (relative intensity) 2.06 (17, M^+), 94 (100, PhOH). Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.43; H, 8.96.

***trans*-1-Phenyl-2-phenoxycyclohexan-1-ol (43)**: crystals; 74%; mp 89 °C (petroleum ether); GLC at 200 °C; IR 1500, 1600 (Ph), 3450, 3550 cm^{-1} (OH); ^1H NMR δ 1.27–2.13 (8 H, 4 CH_2), 2.81 (s, 1 H, OH), 4.58 (dd, 1 H, J = 5, 11 Hz, 2-H), 6.66–7.57 (10 H, Ph); mass spectrum, m/e (relative intensity) 268 (45, M^+), 94 (36, PhOH). Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.38; H, 7.38.

***trans*-4-*tert*-Butyl-*cis*-2-phenoxycyclohexan-1-ol (46).** Chromatography (CH_2Cl_2–CH_3COCH_3, 99:1) first gave *trans*-5-*tert*-butyl-*cis*-2-phenoxycyclohexan-1-ol: 2%; ^1H NMR ($CDCl_3$, D_2O) δ 4.17 (br, 1 H, 1-H), 4.37 (m, 1 H, J = 3.5, 3.5, 11 Hz, 2-H), 6.78–7.38 (5 H, Ph). Continued elution gave ether **46**: 73%; mp 108 °C (ether–petroleum ether); ^1H NMR ($CDCl_3$, D_2O) δ 3.64 (m, 1 H, J = 3.5, 3.5, 11.5 Hz, 1-H), 4.53 (br s, 1 H, 2-H), 6.78–7.38 (5 H, Ph). Anal. Calcd for $C_{16}H_{24}O_2$: C, 77.37; H, 9.74. Found: C, 77.61; H, 9.64.

***cis*-5-*tert*-Butyl-*trans*-2-Phenoxycyclohexan-1-ol (48) and *trans*-4-*tert*-Butyl-*trans*-2-phenoxycyclohexan-1-ol (49).** Chromatography (hexane–ethyl acetate, 17:3) first gave one isomer (**48** or **49**; 42%): mp 65 °C (petroleum ether); ^1H NMR ($CDCl_3$, D_2O) δ 3.68 (octet, 1 H, J = 5.85, 11.5 Hz, CHOH), 4.05 (octet, 1 H, J = 3.5, 8, 11 Hz, CHOPh), 6.84–7.40 (5 H, Ph). Anal. Calcd for $C_{16}H_{24}O_2$: C, 77.37; H, 9.74. Found: C, 76.96; H, 9.67.

Continued elution gave the second isomer (**49** or **48**, 45%): mp 82 °C (petroleum ether); ^1H NMR ($CDCl_3$, D_2O) δ 3.70 (octet, 1 H, J = 4, 8.5, 10.5 Hz, CHOH), 3.94 (octet, 1 H, J = 4, 8.5, 10.5

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Hz, CHOPh), 6.85–7.34 (5 H, Ph). Anal. Calcd for $C_{16}H_{24}O_2$: C, 77.37; H, 9.74. Found: C, 77.32; H, 9.66.

3α-Phenoxycholestan-2α-ol (51) was prepared from diol **50**.[29] Chromatography (CH_2Cl_2) gave ether **51**: liquid; 60%; ^1H NMR δ 2.14 (d, 1 H, OH), 3.82 (m, 1 H, J = 3.5, 3.5, 11, 11 Hz, 2-H), 4.54 (br s, 1 H, 3-H), 6.88–7.34 (5 H, Ph). Anal. Calcd for $C_{33}H_{52}O_2$: C, 82.44; H, 10.90; O, 6.66. Found: C, 81.80; H, 10.76; O, 6.47.

For the 2-acetate (acetic anhydride, pyridine): ^1H NMR δ 4.70 (br s, 1 H, 3-H), 5.00 (m, 1 H, 2-H).

Reaction with Cholestane-2α,3β-diol (52).[30] Chromatography (CH_2Cl_2–acetone, 99:1) separated a 1:1 mixture of **53** and **54** (11%): ^1H NMR δ 3.72 (octet, 1 H, CHOH), 3.90 (o, 1 H, CHOH), 3.96 (octet, 1 H, CHOPh), 4.22 (octet, 1 H, CHOPh), 6.77–7.38 (10 H, Ph).

Benzyl 2,3-Di-*O*-benzyl-4-*O*-phenyl-α-D-glucopyranoside (56) and Benzyl 2,3-Di-*O*-benzyl-6-*O*-phenyl-α-D-glucopyranoside (57). The starting diol was **55**.[31] Chromatography (CH_2Cl_2–acetone, 97:3) first gave ether **57**: syrup; 15%; ^1H NMR δ 2.40 (1 H, OH), 3.88 (pst, 1 H, $J_{3,4} = J_{4,5}$ = 9 Hz, 4-H), 4.13 (m, 2 H, 6-H, 6′-H), 6.78–7.30 (20 H, Ph). Anal. Calcd for $C_{33}H_{34}O_6$: C, 75.26; H, 6.51; O, 18.23. Found: C, 75.08; H, 6.77; O, 18.15.

Continued elution gave ether **56**: 13%; mp 94 °C (petroleum ether); ^1H NMR δ 1.70 (1 H, OH), 3.66 (m, 2 H, 6-H, 6′-H), 4.40 (pst, 1 H, $J_{3,4} = J_{4,5}$ = 9 Hz, 4-H), 6.80–7.50 (20 H, Ph). Anal. Calcd for $C_{33}H_{34}O_6$: C, 75.26; H, 6.51; O, 18.23. Found: C, 75.13; H, 6.55; O, 17.97.

Benzyl 4,6-*O*-Benzylidene-2-*O*-phenyl-α-D-mannopyranoside (60) and Benzyl 4,6-*O*-Benzylidene-3-*O*-phenyl-α-D-mannopyranoside (61). These were prepared from mannoside **59**.[32] Chromatography (dichloromethane–acetone, 99:1) first gave **60**: crystals; 42%; mp 133 °C (ether–petroleum ether); ^1H NMR δ 2.76 (1 H, OH), 4.22 (dd, 1 H, $J_{2,3}$ = 3.5, $J_{3,4}$ = 10 Hz, 3-H), 4.56 (d, 1 H, 2-H), 5.00 (s, 1 H, 1-H), 6.78–7.58 (15 H, Ph). Anal. Calcd for $C_{26}H_{26}O_6$: C, 71.87; H, 6.03; O, 22.10. Found: C, 71.60; H, 6.01; O, 22.20.

For the 3-acetate (acetic anhydride, pyridine): ^1H NMR δ 5.42 (dd, 1 H, $J_{2,3}$ = 3.5, $J_{3,4}$ = 10 Hz, 3-H).

Continued elution gave ether **61**: syrup; 11%; ^1H NMR δ 2.68 (1 H, OH), 4.24 (1 H, 2-H), 4.71 (dd, 1 H, $J_{2,3}$ = 3.5, $J_{3,4}$ = 10 Hz, 3-H), 4.90 (s, 1 H, 1-H), 6.84–7.54 (15 H, Ph). Anal. Calcd for $C_{26}H_{26}O_6$: C, 71.87; H, 6.03; O, 22.10. Found: C, 71.60; H, 6.08; O, 22.11.

For the 2-acetate (acetic anhydride, pyridine): ^1H NMR δ 5.42 (dd, 1 H, $J_{1,2}$ = 1, $J_{2,3}$ = 3.5 Hz, 2-H).

Benzyl 3-*O*-Phenyl-6-*O*-trityl-α-D-mannopyranoside (63). Chromatography (CH_2Cl_2–acetone, 99:1) of the product of phenylation of triol **62**[33] first gave ether **63**: syrup; 32%; ^1H NMR δ 2.52 (1 H, OH), 2.74 (1 H, OH), 3.48 (d, 1 H, $J_{2,3}$ = 3.5 Hz, 2-H), 4.93 (1 H, 1-H), 5.51 (dd, 1 H, $J_{3,4}$ = 10 Hz, 3 H), 6.78–7.52 (25 H, Ph).

For the 2,4-diacetate (acetic anhydride, pyridine): ^1H NMR δ 1.65 (s, 3 H, Ac), 2.16 (s, 3 H, Ac), 3.10–3.34 (2 H, 6-H, 6′-H), 4.00 (1 H, 5-H), 4.68 (dd, 1 H, $J_{2,3}$ = 3.5, $J_{3,4}$ = 10 Hz, 3-H), 4.98 (d, 1 H, $J_{1,2}$ = 1 Hz, 1-H), 5.40 (pst, 1 H, $J_{3,4} = J_{4,5}$ = 10 Hz, 4-H), 5.40 (d, 1 H, 2-H), 6.78–7.52 (25 H, Ph).

Continued elution gave a mixture of other phenyl ethers (yield 23%).

Benzyl 2,3-Di-*O*-benzyl-4-*O*-phenyl-β-D-galactopyranoside (65) and Benzyl 2,3-Di-*O*-benzyl-6-*O*-phenyl-βD-galactopyranoside (66). The starting material was diol **64**.[34] Chromatography (CH_2Cl_2–acetone, 97:3) first gave ether **66**: syrup; 11%; ^1H NMR δ 2.53 (1 H, OH), 4.10 (d, 1 H, $J_{3,4}$ = 3.5 Hz, 4-H), 4.28 (m, 2 H, 6-H, 6′-H), 6.87–7.42 (m, 20 H, Ph). Anal. Calcd for $C_{33}H_{36}O_6$: C, 75.26; H, 6.51; O, 18.23. Found: C, 75.02; H, 6.64; O, 18.29.

Continued elution gave **65**: crystals; 26%; mp 103 °C (ether–petroleum ether); ^1H NMR δ 2.10 (1 H, OH), 3.70 (m, 1 H, 6-H), 3.86 (m, 1 H, 6′-H), 4.62 (d, 1 H, $J_{3,4}$ = 3.5 Hz, 4-H), 6.76–7.40 (20 H, Ph). Anal. Calcd for $C_{33}H_{34}O_6$: C, 75.26; H, 6.51; O, 18.23. Found: C, 75.41; H, 6.45; O, 18.49.

Benzyl 2,6-Di-*O*-benzyl-3-*O*-phenyl-α-D-galactopyranoside (68) and Benzyl 2,6-Di-*O*-benzyl-4-*O*-phenyl-α-D-galactopyranoside (69). The starting material was diol **67**.[35] Chromatography (CH_2Cl_2–acetone, 99:1) first gave **68**: syrup; 4%; ^1H NMR δ 5.02 (d, 1 H, $J_{1,2}$ = 4 Hz, 1-H). Anal. Calcd for $C_{33}H_{34}O_6$: C, 75.26; H, 6.51; O, 18.23. Found: C, 75.24; H, 6.64; O, 18.01.

For the 4-acetate (acetic anhydride, pyridine): ^1H NMR δ 2.05 (s, 3 H, Ac), 4.93 (d, 1 H, J = 4 Hz, 1-H), 5.55 (d, 1 H, $J_{3,4}$ = 3.5 Hz, 4-H), 6.80–7.30 (20 H, Ph).

Continued elution gave ether **69**: crystals; 30%; mp 67 °C (ether, petroleum ether); ^1H NMR δ 3.52 (2 H, 6-H, 6′-H), 3.88 (dd, 1 H, $J_{1,2}$ = 3, $J_{2,3}$ = 10 Hz, 2-H), 4.98 (d, 1 H, 1-H), 6.80–7.30 (20 H, Ph). Anal. Calcd for $C_{33}H_{34}O_6$: C, 75.26; H, 6.51; O, 18.23. Found: C, 74.97; H, 6.63; O, 18.40.

For the 3-acetate (acetic anhydride, pyridine): ^1H NMR δ 2.10 (s, 3 H, Ac), 4.10 (dd, 1 H, $J_{1,2}$ = 3, $J_{2,3}$ = 11 Hz, 2-H), 4.95 (d, 1 H, 1-H), 5.30 (dd, 1 H, $J_{3,4}$ = 3.5 Hz, 3-H), 6.80–7.40 (20 H, Ph).

Methyl 2-*O*-Allyl-6-*O*-trityl-α-D-allopyranoside (70). A mixture of methyl 2-*O*-allyl-α-D-allopyranoside (0.3 g, 1.3 mmol), triethylamine (0.5 mL), 4-(dimethylamino)pyridine (10 mg), and triphenylmethyl chloride (0.365 g) dissolved in dichloromethane (5 mL) was kept for 16 h at room temperature under nitrogen. Then the solution was poured into a mixture of ice and water and extracted with dichloromethane. The organic layer was washed with a saturated, aqueous, ammonium chloride solution and with water and evaporated to dryness. Chromatography of the residue gave the trityl ether **70**: syrup; 0.31 g, $[\alpha]^{20}_D$ +38° (*c* 1.4, dichloromethane); ^1H NMR (90 MHz) δ 3.50 (3 H, s, Me), 4.90 (1 H, d, $J_{1,2}$ = 4 Hz, 1-H), 6.00 (1 H, m, CH=), 7.30–7.60 (15 H, 3 Ph). Anal. Calcd for $C_{29}H_{32}O_6$: C, 73.09; H, 6.77; O, 20.14. Found: C, 73.01; H, 6.70; O, 20.25.

Methyl 2-*O*-Allyl-3-*O*-phenyl-6-*O*-trityl-α-D-allopyranoside (71). The starting diol was **70**. Chromatography (dichloromethane–acetone, 99:1) first gave traces of ether **72** (3%) and then ether **71**: syrup; 27%; ^1H NMR δ 2.35 (1 H, OH), 3.55 (s, 3 H, Me), 3.62 (pst, 1 H, $J_{1,2} = J_{2,3}$ = 3.5 Hz, 2-H), 4.80 (pst, 1 H, $J_{3,4}$ 3.5 Hz, 3-H), 4.88 (d, 1 H, 1-H), 5.75 (m, 1 H, CH=), 6.88–7.56 (20 H, Ph).

For the 4-acetate (acetic anhydride, pyridine): ^1H NMR δ 3.53 (s, 3 H, Me), 3.74 (pst, 1 H, $J_{1,2} = J_{2,3}$ = 3.5 Hz, 2-H), 4.96 (d, 1 H, 1-H), 5.00 (dd, 1 H, $J_{3,4}$ = 3, $J_{4,5}$ = 10 Hz, 4-H), 5.08 (pst, 1 H, 3-H), 6.72–7.54 (20 H, Ph).

Registry No. **1**, 107-21-1; **2**, 6982-25-8; **3**, 22520-41-8; **4**, 579-43-1; **5**, 76-09-5; **6**, 464-72-2; **7**, 57-55-6; **8**, 93-56-1; **9**, 5396-58-7; **10**, 41728-16-9; **11**, 504-63-2; **12**, 110-63-4; **13**, 111-29-5; **14**, 629-11-8; **15**, 6117-80-2; **16**, 122-99-6; **17**, 81454-96-8; **18**, 84073-47-2; **19**, 81454-98-0; **20**, 81455-02-9; **21**, 770-35-4; **22**, 4169-04-4; **23**, 4249-72-3; **24**, 53574-80-4; **25**, 81455-03-0; **26**, 81455-04-1; **27**, 6180-61-6; **28**, 1927-71-5; **29**, 16654-52-7; **30**, 16654-54-9; **31**, 81455-07-4; **32**, 5057-98-7; **33**, 5057-99-8; **34**, 1792-81-0; **35**, 1460-57-7; **36**, 19534-08-8; **37**, 27167-34-6; **38**, 81454-99-1; **39**, 81455-00-7; **40**, 81455-01-8; **41**, 79251-44-8; **42**, 81455-05-2; **43**, 81455-06-3; **44**, 19793-87-4; **45**, 84073-48-3; **46**, 84073-49-4; **47**, 19793-88-5; **48**, 84073-50-7; **49**, 84073-51-8; **50**, 20312-09-8; **51**, 84073-52-9; **51** 2-acetate, 84073-53-0; **52**, 16126-30-0; **53**, 84073-54-1; **54**, 84073-55-2; **55**, 58527-86-9; **56**, 84073-56-3; **57**, 84073-57-4; **58**, 57701-27-6; **59**, 73366-72-0; **60**, 84073-58-5; **60** 3-acetate, 84073-59-6; **61**, 84073-60-9; **61** 2-acetate, 84073-61-0; **62**, 77455-30-2; **63**, 84073-62-1; **63** 2,4-diacetate, 84073-63-2; **64**, 74801-06-2; **65**, 84073-64-3; **66**, 84073-65-4; **67**, 72045-27-3; **68**, 84073-66-5; **68** 4-acetate, 84073-67-6; **69**, 84073-68-7; **69** 3-acetate, 84073-69-8; **70**, 84073-70-1; **71**, 84073-71-2; **71** 4-acetate, 84073-72-3; **73**, 79549-74-9; methyl 2-*O*-allyl-α-D-allopyranoside, 84073-73-4; triphenylbismuth diacetate, 28899-97-0.