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SYNTHESIS OF GLYCOSYL HALIDES AND GLYCOSIDES *via* 1-*O*-SULFONYL DERIVATIVES

JACQUES LEROUX AND ARTHUR S PERLIN
Department of Chemistry, McGill University, Montreal H3A 2A7 (Canada)
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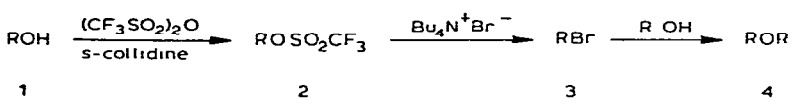
ABSTRACT

The reaction of an aldose derivative containing a free anomeric hydroxyl group with trifluoromethanesulfonic anhydride or methanesulfonic anhydride, in the presence of halide ion and *s*-collidine, furnishes a glycosyl halide, if an alcohol is then introduced, glycoside synthesis is effected in an overall, "one-pot" reaction Several α-D-glucopyranosides including disaccharides, have been prepared in high yield by using 2,3,4,6-tetra-*O*-benzyl-D-glucose as the aldose, and generating the corresponding glycosyl bromide(s) *in situ* As a halide-exchange step is incorporated in the reaction sequence, orthoacetate formation was favored in reactions of 2,3,4,6-tetra-*O*-acetyl-D-glucose, such as occurs with per-*O*-acetylglycosyl halides Methanesulfonic anhydride promotes glycosidation or orthoester formation in the absence of halide ion, as well as in its presence, whereas formation of an intermediate glycosyl halide appears to be necessary in order to moderate the more vigorous reactions of the trifluoro derivative The analogous reaction of methanesulfonyl chloride with an aldose provides a ready route to glycosyl chlorides Under the conditions employed for these various syntheses, acid-sensitive protecting groups may be used, including cyclic and acyclic acetals and *O*-trityl substituents

INTRODUCTION

In an earlier article[1], it was reported that a glycoside (**4**) may be synthesized in high yield from a sugar derivative bearing a free anomeric hydroxyl group (**1**) by direct addition of the appropriate alcohol (R'OH) to a mixture of the sugar, bromide ion, *s*-collidine, and trifluoromethanesulfonic (triflic) anhydride It was proposed that, in the formation of **4**, a glycosyl trifluoromethanesulfonate (triflate) (**2**) and a bromide (**3**) are intermediates, and that the latter undergoes displacement by the alcohol We now provide a fuller description of this synthetic procedure, describe some characteristics of the reactions involved, and deal with the use of related sulfonyl derivatives in the synthesis of halides and glycosides



RESULTS AND DISCUSSION

Synthesis of α-D-glucopyranosides — Initially, an attempt was made to use a 1-triflate (**2**) directly in a reaction with the alcohol, but this was unsuccessful Thus, 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranose[2] (**5**) in cold *s*-collidine–dichloromethane was treated with triflic anhydride According to chromatographic and n m r -spectroscopic evidence, a rapid transformation of **5** took place, giving, presumably*, **6**, but the product was unstable, and the introduction of methanol or ethanol under anhydrous conditions failed to produce an appreciable yield of glycoside

An alternative approach was then examined bromide ion, a more efficient nucleophile than an alcohol, was introduced, so as to allow for the possibility of a rapid reaction with the glycosyl triflate generated from **5** This procedure, employing tetrabutylammonium bromide, afforded a syrupy product that, by p m r spectroscopy, was indistinguishable from 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl bromide (**7**)**, prepared by the reaction of hydrogen bromide with 1-*O*-benzoyl-2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranose (**8**) On monitoring the halogenation reaction by p m r spectroscopy, the transient existence of a product was detected in the form of a relatively weak doublet (J ~4 Hz), appearing 0 1 p p m downfield of the H-1 signal (J 4 0 Hz) of bromide **7** As there was no bromination in the absence of triflic anhydride, it appeared likely that the product detected as an intermediate was the α-triflate (**6**) If displacement by bromide ion then occurred, to give the β-bromide (**9**) initially, isomerization to the thermodynamically more stable α anomer (**7**) would follow, through halide exchange[4 6 7] under the conditions of the reaction***

Based on these observations, an experiment was performed in which a solution of aldose **5** (1 0 mmol), collidine (3 0 mmol), and tetrabutylammonium bromide (2 0 mmol) in dichloromethane was added to triflic anhydride (1 5 mmol), followed, after 1 h, by methanol This afforded methyl 2,3,4,6-tetra-*O*-benzyl-α,β-D-glucopyranoside (**10**, **11**) in an overall yield of 94% ($\alpha/\beta = 13\ 7$)

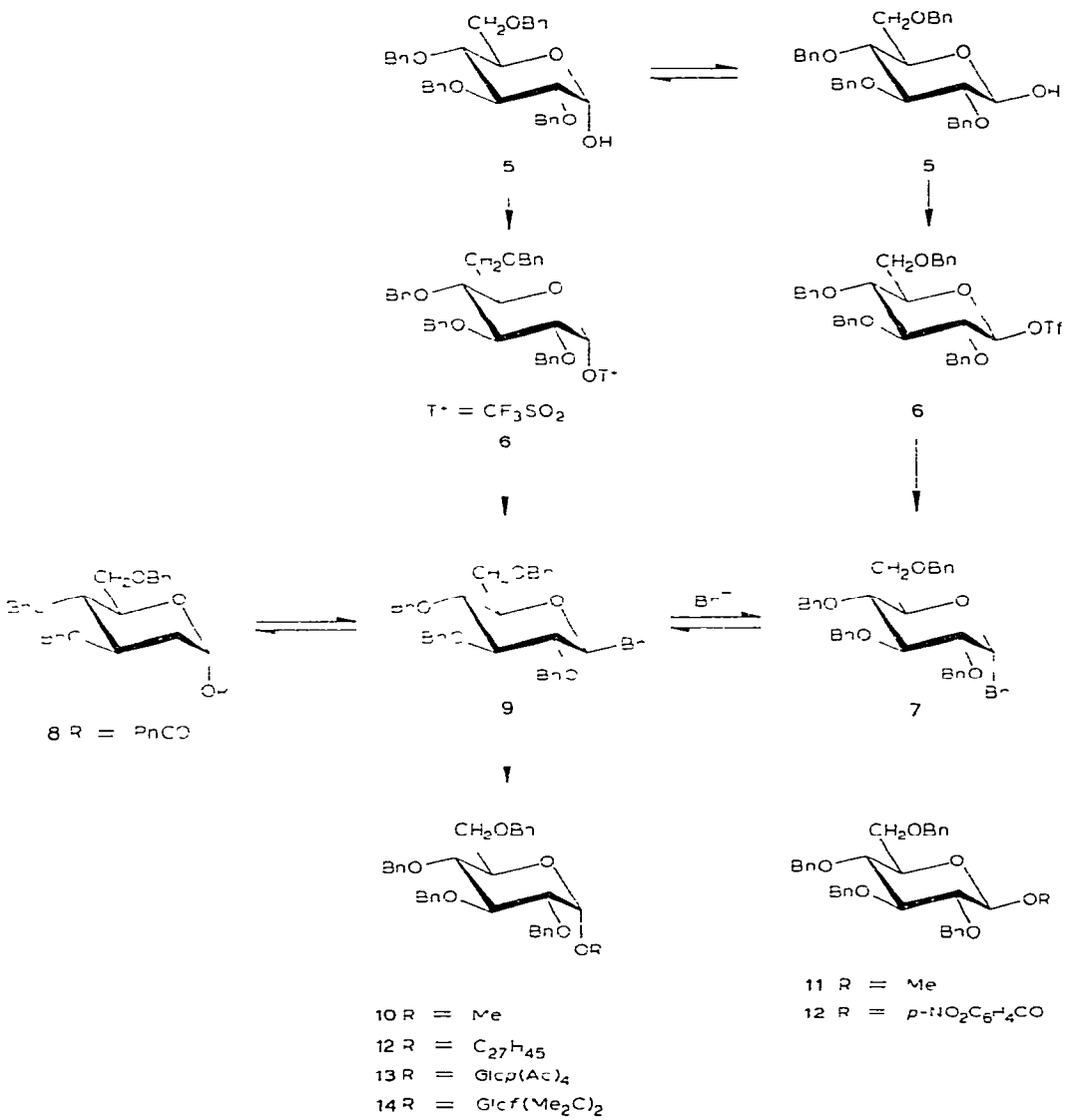
When cholesterol was used as the hydroxylic component instead of methanol, crystalline cholesteryl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside[8] (**12**) was obtained in 62% yield No trace of the β anomer of **12** was found Similarly, with 1,2,3,4-tetra-*O*-acetyl-β-D-glucopyranose, disaccharide **13** [*i e*, 1,2,3,4-tetra-*O*-acetyl-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-β-D-glucopyranose] was isolated in 63% yield, and disaccharide **14** (ref 5) was synthesized in a yield of 85% by the use of 1,2 5,6-di-*O*-isopropylidene-γ-D-glucofuranose as the hydroxylic component According to ^{13}C-n m r -spectroscopic evidence, none of the β anomer of **13** or **14** was produced in these reactions

*Additional evidence for the formation of a 1-triflate is provided later (by the reaction of **5** with pyridine in the presence of triflic anhydride)

Bromide **7 has been described as an unstable syrup by several workers[3–5], who prepared it by other methods

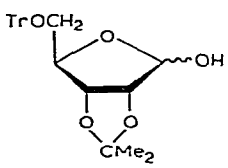
***Bromide **7** should also be produced if some of the β-triflate (**6**) were formed due to anomerization of **5** in solution, according to the n m r spectrum of a solution of **5** in *s*-collidine–$CDCl_3$, however, <10% of the β anomer (**5′**) of **5** is present at equilibrium

These findings indicate, therefore, that an aldose such as **5** may be converted into a glycoside (**10–14**) through the successive intermediacy of a 1-triflate (**6**) and a glycosyl bromide (**7,9**) Due to the presence of an excess of bromide ion in the medium, **7** and **9** are in equilibrium, permitting glycoside formation to take place under kinetic control, *i e*, **9** reacts more rapidly[4–6] with the alcohol, with inversion, favoring synthesis of the α-D-glucoside With cholesterol and the monosaccharide alcohols, α anomers (**12–14**) appear to be formed exclusively Perhaps because of its greater reactivity, methanol is less stereoselective, although the α-D-glycoside (**10**) is still favored by a factor of two



A noteworthy feature of the current procedure is the fact that it circumvents the usual practice of employing the reaction of a hydrogen halide with a 1-*O*-acyl-aldose derivative to generate a glycosyl halide For example, earlier preparations of 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl bromide (**7**) involved[3–5] the conversion of the tetra-*O*-benzylaldose (**5**) into a 1-*O*-acyl derivative (*e g* , **15**), followed by treatment with hydrogen bromide to give **7** Compound **7** was then employed for the synthesis of D-glucosides, *e g* , **13** Thus, compound **5** has now been converted into **13** in a "one-pot" reaction, leading to an improved, overall yield of product, as well as a diminution in both the individual number of steps involved in the synthetic sequence and the time required

Another advantage lies in the feasibility of preparing glycosyl halides bearing acid-labile protecting-groups, because acidic conditions are not employed in the triflation–bromination procedure, For example, when 2,3-*O*-isopropylidene-5-*O*-trityl-D-ribofuranose (**16**), in the presence of *s*-collidine and tetrabutylammonium bromide, was treated with triflic anhydride, followed by methanol, it afforded a 2 1 mixture of the methyl α- and β-glycosides (**17**, **18**) in 64% yield Hence, both the cyclic acetal and *O*-trityl groups were stable under these reaction conditions In an analogous way, methyl 2,3 5,6-di-*O*-isopropylidene-α,β-D-mannofuranoside (**19**, **20**) (α β = 2 3) was obtained from the free aldose*



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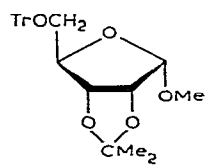

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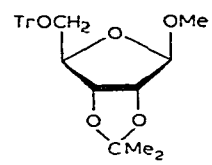

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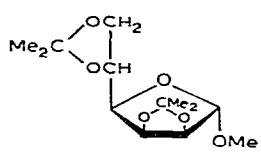

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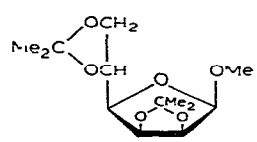

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Some experimental factors — In most of the reactions just described, the triflic anhydride was initially mixed with other components of the reaction mixture at −70° When the bromide had formed (usually, in 15–30 min), its reaction with the alcohol was then conducted at room temperature However, in some instances, the bromide was also generated at room temperature without apparent disadvantage, indicating

*Preliminary experiments with an acyclic acetal protecting group, *viz* , –OCH(OEt)Me, showed that this type of substituent is also stable

that the precaution of working at a low temperature with triflic anhydride may not be necessary All of these reactions were accompanied by the development of a dark color (from unidentified by-products), although there was substantially less coloration at −70° (which, initially, prompted the choice of a low temperature) Column chromatography on silica gel was highly effective in decolorization of the reaction products

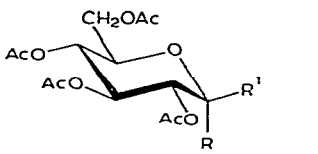
The question of stoichiometry in these reactions merits comment For each mole of the aldose, one mole of triflic anhydride is needed in order to promote the conversion into a glycosyl bromide and, subsequently, by introduction of an aglycon alcohol, into a glycoside It may be advantageous to use a small excess of anhydride, to counter traces of moisture in the system and also to favor formation of the triflate However, unreacted anhydride could then be present when the alcohol is added When the aglycon is derived from a readily available alcohol, this practice is warranted However, if the aldose is relatively accessible (*e g* , **5**) and the alcohol is the more expensive compound, the use of no more than one molar proportion of triflic anhydride is advisable, *i e* , the yield based upon the aglycon moiety should be improved

Reactions involving neighboring-group participation — Experiments with a sugar derivative having a free hydroxyl group at C-1, and *O*-acyl, rather than *O*-benzyl, substituents were expected to shed more light on the action of triflic anhydride at the anomeric center

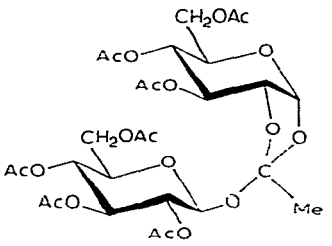
When a solution of 2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranose (**21**) (1 mmol) in collidine (3 mmol) and dichloromethane was added to triflic anhydride (1 5 mmol), a rapid reaction took place, giving a disaccharide" orthoester (**22**) as the main product (44% yield) The p m r spectrum of **22** exhibited a 3-proton singlet at 1 7 p p m due to the C-CH_3 group, a value characteristic of an *exo* orientation of -OR in 1,2-orthoacetates[10] The presence of 12 carbon atoms in two sugar moieties, as well as of the *C*-methyl group and 7 carbonyl groups, appropriate to structure **22** was confirmed by ^{13}C-n m r spectroscopy According to the ^{1}H-coupled ^{13}C spectrum, which clearly demonstrated the presence of the quaternary carbon atom in **22**, $^{1}J_{C\,1-H\,1}$ of the glycosyl group is 162 Hz, which is indicative[11 12] of a *β-gluco* configuration for that moiety Optical rotatory data were also consistent with the structure shown

Probably, the synthesis of this disaccharide orthoester originates in the formation of the *β*-triflate (**23**) from **21** With participation of OAc-2, a cyclic acetoxonium ion (**24**) can be generated, and this may undergo attack from as-yet-unreacted aldose **21** In the presence of *s*-collidine[13], the *exo* diastereoisomeric orthoester, **22**, would be favored An analogous type of disaccharide orthoester in the D-mannose series, and also a trimeric species, have been encountered[14 15] as side-products of Koenigs–Knorr reactions

In contrast to those dealing with 2,3,4,6-tetra-*O*-benzyl-D-glucose (**5**), the reaction just described was performed in the *absence* of bromide ion Apparently, the aldose itself (**21**) is a sufficiently good nucleophile to react with a triflate (**23**) as it is formed Bromide ion, however, should capture the triflate much more efficiently than **21**, this proved to be true with the introduction of tetrabutylammonium bromide,



21 R = H R¹ = OH
23 R = H, R¹ = OSO_2CF_3
25 R = Br R¹ = H



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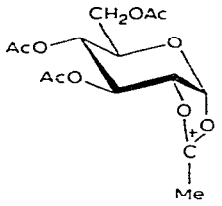

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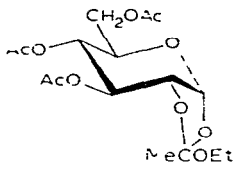

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crystalline 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide (**25**) was obtained as the major product (50% yield) and there was no indication that orthoester **22** had been formed Furthermore, when ethanol was added to a solution of the aldose (**21**) *s*-collidine, tetrabutylammonium bromide and triflic anhydride in dichloromethane, the expected ethyl 1,2-orthoacetate was obtained in 66% yield this product consisted of a 7 1 mixture of the *exo* and *endo* diastereoisomers, from which the *exo* species[7] (**26**) was isolated in crystalline form That is, as the bromide (**25**) was undoubtedly generated *in situ*, the conventional formation of a 1 2-orthoacetate (*via* **24**) could proceed

Reactions of methanesulfonic anhydride at the anomeric center — In view of the facility with which triflic anhydride induces reactivity at the anomeric center of aldoses, it was of interest to examine the behavior of other sulfonic acid derivatives One such derivative is methanesulfonic (mesic) anhydride which is a crystalline, commercially available compound

To parallel the reactions with triflic anhydride, a solution of 2,3 4,6-tetra-*O*-benzyl-α-D-glucopyranose (**5**, 0 5 mmol), *s*-collidine (2 0 mmol), and tetrabutylammonium bromide (1 0 mmol) in dichloromethane (2 5 mL) was added to mesic anhydride (1 5 mmol), and then to methanol Column chromatography of the reaction mixture afforded a 7 3 mixture of the methyl α- and β-glycosides (**10** and **11**) in 61% overall yield Moreover, the use of the same experimental conditions, but without inclusion of the bromide ion, again produced a mixture (3 2) of **10** and **11**, in 87% yield

The latter finding indicates that a 1-mesylate, in contrast to a 1-triflate, is sufficiently stable to allow for a displacement reaction by the alcohol The fact that

the α-glucoside (**10**) is the preponderant product in all of these reactions with **5** suggests that, as with a glycosyl halide, the intermediate mesylate undergoes anomeric equilibration (**27**⇌**28**), and that a more rapid displacement occurs with the β anomer to give, with inversion, the α-glycoside

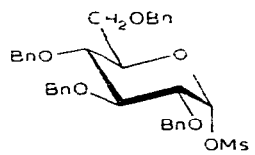
The reaction of 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranose with mesic anhydride gave a crystalline product (74% yield), which had a m p (108–110°) and specific rotation (+124°) close to those (112–113°, +121°) of a 1-*O*-mesyl compound prepared[16] from 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide and silver mesylate Although formation of a β-mesylate would have been expected[17] in the silver-catalyzed reaction, a value of 3 Hz for $J_{H\,1-H\,2}$ for the current product showed that both preparations must have the α configuration, a designation also in accord with the high, positive rotation observed for both

By incorporating ethanol into a reaction mixture consisting of 2 3,4,6-tetra-*O*-acetyl-β-D-glucopyranose, *s*-collidine, and mesic anhydride, a quantitative yield of orthoester **26** admixed with 10% of the *endo* isomer was obtained

Overall, these reactions bear a substantial resemblance to those employing triflic anhydride Differences appear to arise from the greater stability of a mesylate than of a triflate Accordingly, in the latter series, it was found necessary to moderate reactions by converting the triflate into the corresponding bromide Glycoside synthesis occurs smoothly in both series when non(or weakly[18])-participating *O*-benzyl groups are present yielding a preponderance of α-anomeric products, whereas orthoesters are formed with *O*-acetyl substituents through neighboring-group participation

Reactions of sulfonyl chlorides at the anomeric center — By analogy with the triflic and mesic anhydride reactions, when 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranose (**5**) collidine, and tetrabutylammonium bromide in dichloromethane were mixed with methanesulfonyl (mesyl) chloride, and methanol was introduced, the product was a mixture of methyl 2,3,4,6-tetra-*O*-benzyl-α- and -β-D-glucopyranosides (**10** and **11** α β = 4 1 80% yield)

Although the bromide **7** would be expected to be an intermediate, chloride ion liberated during the reaction might also affect the anomeric position In fact the addition of mesyl chloride to a solution of **5** and *s*-collidine in dichloromethane gave a syrupy product (63% yield) which, according to n m r -spectral and optical rotatory data, was 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl chloride (**29**) It is known[19] that glycosyl bromides undergo rapid displacement with chloride ion and, in accordance with this fact, the addition of tetrabutylammonium bromide to a solution of **29** in



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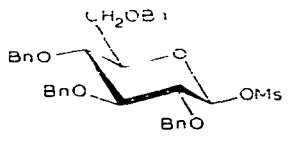

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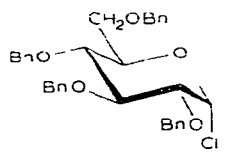

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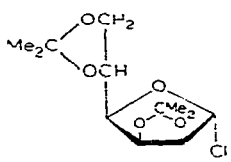
dichloromethane had no detectable effect (n m r evidence) Hence, it is possible that, in the formation of **10** and **11** (see preceding paragraph), methanol enters into reaction simultaneously with 1-bromo, 1-chloro, and 1-mesyl intermediates

p-Toluenesulfonyl chloride reacted much more slowly than mesyl chloride with **5**, although it, too, afforded the glycosyl chloride **29** (yield, 42%)

Chlorination of C-1 during attempted *O*-sulfonylation of carbohydrates had been observed in earlier studies For example, the reaction of mesyl chloride with D-glucose in pyridine yielded 2,3,4,6-tetra-*O*-mesyl-D-glucosyl chloride[16], and the corresponding *O*-tosyl derivative was also prepared[20], although it was formed much more slowly (Perhaps, a related observation[21], in 1870, concerned the isolation of tetra-*O*-acetyl-D-glucosyl chloride from the reaction between D-glucose and acetyl chloride)

The stability of acetal substituents to this chlorination reaction was demonstrated by treating 2,3 5,6-di-*O*-isopropylidene-α-D-mannofuranose with mesyl chloride in *s*-collidine–dichloromethane, this afforded, after chromatographic purification, the α-chloro derivative (**30**) in 72% yield Compound **30** has also been prepared[22] from the aldose by the use of thionyl chloride and, very recently, through the action of dichlorocarbene generated[23] in a phase-transfer* system



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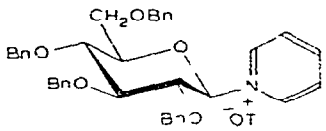
Relationship to silver sulfonate-modified reactions — Glycoside synthesis by the sequence of reactions described here is, in part, the converse of that introduced by Schuerch and co-workers[25,26], which employs silver sulfonates to mediate the reaction between an alcohol and a glycosyl halide In both sequences, 1-*O*-sulfonyl derivatives are plausible intermediates However, our conditions are generally more favorable for glycoside synthesis when bromide ion is present, whereas halide ion is removed from the medium when the silver salt is used As a consequence, the procedure described here favors a halide-exchange step and, therefore, the formation of α-D-glucosides With silver sulfonates, the stereoselectivity can be varied widely, depending on such factors as the solvent and the nature of the substituent groups on the glycosyl halide An elegant example is the recent synthesis[27] of α anomers in the isomalto-oligosaccharide series, employing silver *p*-toluenesulfonate and 2,3,4-tri-*O*-benzyl-6-*O*-(*N*-phenylcarbamoyl)-α-D-glucopyranosyl chloride Alternatively, the use of silver triflate (and an acid acceptor) with per-*O*-acyl-D-glucopyranosyl halides has

*A related type of reaction is the preparation of (alkyloxy)glycosylphosphonium salts from aldoses for use in the synthesis of glycosides[24]

been shown by Hanessian and Banoub[28,29] to give excellent yields of β-D-glucosyl disaccharides

The current study furnishes a procedure for the preparation of glycosyl halides from aldoses, and hence supplements the general chemistry of syntheses involving glycosyl halides For applications in the synthesis of glycosides, the procedure offers several advantages when an aldose is a suitable starting-material Among these is the fact that the glycosyl halide is generated *in situ* under conditions conducive to a high yield of α-glycoside, and that acid-labile substituent groups may be employed

*Formation of 1-(2,3,4,6-tetra-*O*-benzyl-β-*D*-glucopyranosyl)pyridinium trifluoromethanesulfonate* (**31**) — In a preliminary attempt to prepare a 1-*O*-sulfonyl derivative[30], 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranose (**5**) was dissolved in pyridine, and a 1 5-fold excess of triflic anhydride was introduced After 20 min, the reaction was quenched with water, and the product extracted into chloroform, and subsequently crystallized Instead of the 1-triflate (**3**) expected, however, this product (50% yield) proved to be 1-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)pyridinium triflate (**31**) Among other data supporting formulation **31** is ^{13}C-n m r evidence for the presence



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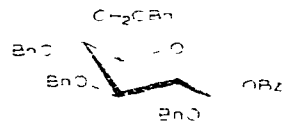

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of a trifluoromethyl group, *i e* , a quartet exhibiting $^{1}J_{C-F}$ 320 Hz (triflic acid gives $^{1}J_{C-F}$ 315 Hz) The β configuration is indicated by the fact that the H-1 signal of **31** is a doublet, $J_{1,2}$ 8 5 Hz, and that the specific rotation of **31** is −20°

In examining some properties of **31**, it was found that the compound undergoes displacement when heated under reflux in *N*,*N*-dimethylformamide with sodium benzoate, to give 1-*O*-benzoyl-2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranose (**32**) Also, as has been observed with other pyridinium triflates, it readily afforded the analogous (crystalline) iodide upon treatment with sodium iodide

The tendency of glycosyl halides to quaternize in pyridine has been known[7,31] for many years Also, pyridinium *p*-toluenesulfonates have been obtained[32] by the reaction of pyridine and silver *p*-toluenesulfonate with halogen derivatives of carbohydrates More recently, Hall and Miller[33] described the formation of 1-(6-deoxy-1,2 3,4-di-*O*-isopropylidene-α-D-galactopyranos-6-yl)pyridinium triflate by the action of triflic anhydride in pyridine on 1,2 3 4-di-*O*-isopropylidene-α-D-galactopyranose The synthesis of **31** is another example of this reaction it appears that aldose **5** rapidly yields a 1-triflate (**6**), which reacts with pyridine to give the pyridinium triflate salt (**31**)

Because pyridine so readily forms quaternary salts in the presence of triflic anhydride, its use was avoided in the subsequent experiments However, 2,6-dimethyl-

pyridine shows[13] little tendency to quaternize with glycosyl halides, and as 2,4,6-trimethylpyridine (*s*-collidine) is an even more hindered base[34], it was employed as the acid acceptor, as already indicated

EXPERIMENTAL

General — Evaporations were conducted at 40°, or lower, *in vacuo* Melting points are corrected Optical rotations were measured at 23 ±2° P m r spectra were recorded at 100 MHz with a Varian HA-100 spectrometer ^{13}C-N m r spectra were recorded at 22 63 MHz with a Bruker WH-90 spectrometer Glass plates coated with silica gel G were used for thin-layer chromatography (t l c), usually, the solvents were chloroform, 9 1 chloroform–ether, or 9 1 chloroform–acetone Column chromatography was performed with MN silica gel (0 05–0 2 mm particle size) or E Merck silica gel 60 (0 06–0 2 mm particle size) *s*-Collidine, pyridine, and *N*,*N*-dimethylformamide were distilled from barium oxide, and stored over molecular sieves Other solvents were dried with molecular sieves Triflic anhydride was prepared by mixing trifluoromethanesulfonic acid (3 M Co) with an equal weight of phosphorus pentaoxide and, after 1 h collecting the anhydride (b p 80–82°) by distillation (*caution* the fumes of triflic acid and anhydride are very corrosive)

*1-(2,3,4,6-Tetra-*O*-benzyl-β-*D*-glucopyranosyl)pyridinium trifluoromethanesulfonate* (**31**) — A solution of compound **5** (21 g) in pyridine (40 mL) was added during 5 min to triflic anhydride (23 g) contained in a stoppered flask and cooled to 0° After 20 min, ice water was added, the mixture was extracted with chloroform, and the extract was washed successively with M hydrochloric acid and water, and evaporated A crystalline residue (14 2 g, 49%) was obtained that, after two recrystallizations from petroleum ether–ethanol, had m p 151–151 5°, $[\alpha]_D$ −20 1° (*c* 4, chloroform) p m r data δ 5 8 (d, 1 H, H-1, $J_{1,2}$ 8 5 Hz), 3 6–5 0 (14 H H-2–H-6,6′, 4 CH_2) 7 7, 8 3, and 8 7 [H-β, -γ, -α (pyridinium)], ^{13}C-n m r data δ 93 7 (1 C, C-1), 68 3, 73 3, 74 5, 75 0, 75 6, 77 0, 78 1, 80 1, 84 8 (10 C, C-2–C-6 4 CH_2) 126 9, 127 6, 127 8, 128 0, 128 3, 128 6, 129 2, 136 2, 137 5, 137 7 (26 C, 4 C_6H_5, pyridinium β-C), 141 7 (2 C, pyridinium α-C), and 147 5 (1 C, pyridinium γ-C)

Anal Calc for $C_{40}H_{40}F_3NO_8S$ C, 63 9, H 5 3, F, 7 6, N, 1 9, S, 4 3 Found C, 63 7, H, 5 2, F, 8 3, N, 2 0, S, 4 5

Another preparation of **31** was made by adding a solution of **5** (0 14 g) and pyridine (0 3 g) in dichloromethane (1 mL) to triflic anhydride (0 48 g) at −70° Processing as described afforded a solid product (0 13 g, 70%), m p 149–150°, the p m r spectrum was indistinguishable from that of **31** prepared at 0°

*1-*O*-Benzoyl-2,3,4,6-tetra-*O*-benzyl-β-*D*-glucopyranose* (**32**) — Compound **31** (1 34 g, 1 78 mmol), sodium benzoate (0 43 g, 3 mmol), and *N*,*N*-dimethylformamide (5 mL) were stirred for 70 h at room temperature without apparent reaction (t l c), the mixture was then boiled under reflux for 70 h, and cooled Chloroform was added, the organic layer was washed with water, and evaporated, and the resulting red oil was purified by column chromatography (solvent, chloroform) The first fractions

contained the title compound (0 53 g, 46% yield), m p 96–96 5°, after three recrystallizations from ethanol, it had $[\alpha]_D$ −17 4° (*c* 3 4, chloroform), p m r data δ 6 1 (1 H, H-1, $J_{1,2}$ 8 0 Hz), ^{13}C-n m r data δ 94 8 (1 C, C-1) and 164 8 (1 C, C=O)

Anal Calc for $C_{41}H_{40}O_7$ C, 76 4, H, 6 3 Found C, 76 5, H, 6 1

Continued elution of the column afforded compound **5** (0 47 g), m p 150–152° $[\alpha]_D$ +20 5° (*c* 3 2, chloroform)

1-(2,3,4,6-Tetra-O-benzyl-β-D-glucopyranosyl)pyridinium iodide — A solution of compound **31** (0 6 g) and sodium iodide (1 50 g) in acetone (10 mL) was boiled under reflux for 3 h The acetone was evaporated off, chloroform was added, crystals of sodium iodide were removed by filtration, and the filtrate was evaporated The resulting syrup gave yellow crystals (0 53 g, 91% yield) from ethanol, m p 148–150°, after recrystallization m p 151–152°, $[\alpha]_D$ −19° (*c* 3 1, chloroform) p m r data δ 6 6 (1 H H-1 $J_{1,2}$ 8 0 Hz), ^{13}C-n m r data δ 92 7 (C-1) (other data close to those for **31**)

Anal Calc for $C_{39}H_{40}INO_5$ C, 64 2, H, 5 3, I, 17 4 Found C, 64 1, H, 5 7, I 18 3

1-O-Benzoyl-2,3,4,6-tetra-O-benzyl-α-D-glucopyranose (**8**) — Benzoyl chloride (5 mL) was added to a solution of compound **5** (4 0 g) in pyridine (24 mL) at 0° After 20 h chloroform was added and the solution was washed successively with 1 5M sulfuric acid, saturated sodium hydrogencarbonate solution, and water, and evaporated to afford a solid residue that was recrystallized from methanol (3 7 g 78%) according to its p m r spectrum, this product consisted of a 9 1 mixture of the α and β anomers Repeated recrystallization from methanol gave 2 0 g of pure **8** m p 79 5–80 5°, $[\alpha]_D$ −62 5° (*c* 2 9, chloroform) p m r data δ 6 6 (1 H, H-1, $J_{1,2}$ 2 0 Hz) ^{13}C-n m r data δ 68 2, 73 1, 73 3, 73 7, 75 5, 75 7 77 1 79 1 81 9 (C-2–C-6 and 4 CH_2), 90 7 (C-1), 127 9, 128 0, 121 1 128 4 129 9, 130 0 133 4 137 8 138 0 138 2, 138 8 (5 C_6H_5), and 165 0 (C=O)

Anal Calc for $C_{41}H_{40}O_7$ C 76 4 H, 6 2 Found C 76 1 H, 6 4

2,3,4,6-Tetra-O-benzyl-α-D-glucopyranosyl bromide (**7**) — The benzoate **8** (0 3 g) was added to a saturated solution of hydrogen bromide in dichloromethane (5 mL) After 1 h the solution was evaporated, and the p m r spectrum (solvent $CDCl_3$) of the residual oil was recorded immediately p m r data δ 3 2–5 0 (m, 14 H H-2–6′ and 4 CH_2), 6 4 (1 H H-1 $J_{1,2}$ 4 Hz), and 7 0–7 6 (m, 20 H 4 C_6H_5)

2,3,4,6-Tetra-O-benzyl-α-D-glucopyranosyl bromide (**7**) *via triflic anhydride* — A solution of compound **5** (0 27 g, 0 5 mmol), s-collidine (0 25 g, 2 0 mmol), and tetrabutylammonium bromide (0 32 g, 1 0 mmol) in dichloromethane (2 5 mL) was added to triflic anhydride (0 27 g, 1 0 mmol) at −70° The mixture was allowed to warm to room temperature (t l c then showed that all of the **5** had reacted) and diluted with dichloromethane, and the solution was rapidly passed through a column of silica gel Immediate evaporation of the effluent afforded an oil, the p m r spectrum of which was virtually indistinguishable from that of **7** (see preceding section) As reported by several workers[3–5], the product decomposed rapidly

Methyl 2,3,4,6-tetra-O-*benzyl*-α,β-D-*glucopyranoside* (**10, 11**) — Triflic anhydride (0 42 g, 1 5 mmol) was placed in a septum-sealed flask in a dry box, and then the flask was removed, and cooled to −70° A solution of compound **5** (0 54 g, 1 0 mmol), *s*-collidine (0 36 g, 3 0 mmol), and tetrabutylammonium bromide (0 64 g, 2 0 mmol) in dichloromethane (5 mL) was now introduced by means of a syringe After 5 min, t l c showed that virtually all of the **5** had been converted into a faster-moving compound. the mixture was allowed to warm to room temperature, and methanol (0 6 mL, 15 mmol) was added One hour later, the solution was diluted with chloroform, washed successively with M hydrochloric acid, M sodium hydrogencarbonate, and water, and evaporated Column chromatography of the residue (solvent, 9 1 chloroform–ether) afforded an oil (0 52 g, 94%) which, according to n m r spectroscopy, consisted of a 3 2 mixture of methyl 2,3,4,6-tetra-*O*-benzyl-α- and -β-D-glucopyranoside (**10** and **11**) this anomeric ratio was based on the relative intensities of the methoxyl resonances ^{1}H, δ 3 3 (α) and 3 5 (β), ^{13}C, δ 55 1 (α), 57 0 (β), with reference to the corresponding spectra of authentic α-D-glucoside **10** The major signals in the ^{13}C-n m r spectrum of the mixture [*e g*, δ 98 2 (C-1)] coincided in chemical shift with those of authentic **10** Other signals [δ 10 47 (C-1), 84 7, 82 4, 82 2, 79 5, 78 5, 77 1, 74 7, 73 5, and 69 0] were attributed to C-1–C-6 and 4 CH_2 of **11**

Cholesteryl 2,3,4,6-tetra-O-*benzyl*-α-D-*glucopyranoside* (**12**) — A solution of **5** (0 54 g, 1 0 mmol), *s*-collidine (3 2 mmol) and tetrabutylammonium bromide (0 64 g, 2 0 mmol) in dichloromethane (5 mL) was added to triflic anhydride (0 33 g, 1 2 mmol) at −70° After 5 min, cholesterol (0 58 g, 1 5 mmol) was added, and, after 36 h at room temperature, the mixture was processed as for compounds **10** and **11** Column chromatography afforded a crystalline product (0 57 g, 62%), m p (after 2 recrystallizations from ethanol–ethyl acetate) 137 5–138 5°, $[\alpha]_D$ +47° (*c* 4, chloroform), (lit[8] m p 127–128°, $[\alpha]_D$ +40°), ^{13}C-n m r data δ 68 8, 70 2, 73 0, 73 5, 75 1, 75 6, 76 9, 78 1, 78 4, 82 2 (C-2–6, 4 CH_2), 94 8 (C-1), 127 7, 127 9, 128 1, 128 4 (4 phenyl, C-2–6), 138 2, 138 4 (2 C), and 139 1 (phenyl C-1), signals for the cholesteryl aglycon moiety had almost the same chemical shifts as the 26 signals reported for cholesteryl methyl ether[35]

1,2,3,4-Tetra-O-*acetyl-6*-O-(*2,3,4,6-tetra*-O-*benzyl*-α-D-*glucopyranosyl*)-β-D-*glucopyranose* (**13**) — Using the same procedure as for the synthesis of **12**, 1,2,3,4-tetra-*O*-acetyl-β-D-glucopyranose (0 35 g, 1 0 mmol) was added to a mixture of **5** (0 27 g, 0 5 mmol), *s*-collidine (0 30 g, 2 5 mmol), tetrabutylammonium bromide (0 32 g, 1 0 mmol), dichloromethane (5 mL), and triflic anhydride (0 27 g, 1 0 mmol) After 18 h at room temperature, the product was isolated by column chromatography as an oil (0 27 g 63%), $[\alpha]_D$ +32° (*c* 7, chloroform), ^{13}C-n m r data δ 20 5 (4 CH_3), 65 9, 68 6, 69 0, 70 5, 72 9, 73 1, 73 5, 74 8 74 9, 75 6, 77 3, 77 7, 80 0, 81 7 (14 C, C-2–6, C-2′–6′, 4 CH_2), 91 8 (C-1′, β) 97 0 (C-1, α), 127 5, 127 8, 128 0, 128 4 (20 C phenyl C-2–6), 138 1 138 4 138 6, 139 0 (4 C, phenyl C-1), 168 7, 169 1, 169 4, and 170 1 (4 C, C=O)

1,2 5,6-Di-O-*isopropylidene-3*-O-(*2,3,4,6-tetra*-O-*benzyl*-α-D-*glucopyranosyl*)-

α-D-*glucofuranose* (**14**) — The experiment described in the preceding paragraph was repeated, but using 1,2 5,6-di-*O*-isopropylidene-α-D-glucofuranose (0 26 g, 1 0 mmol) as the hydroxylic component instead of tetra-*O*-acetyl-D-glucose A chromatographically pure oil was isolated (0 33 g, 85%), $[\alpha]_D$ +43° (*c* 2, chloforoform) (lit [4] $[\alpha]_D$ +46°), ^{13}C-n m r data δ 25 5, 26 2, 26 8, 27 0 (4 C, CH_3), 67 0, 68 8, 71 3, 72 4, 73 1, 73 6, 75 3, 75 6, 77 8, 80 1, 80 9, 81 2, 81 5, 83 7 (14 C, C-2–6, C-2′–6′, 4 CH_2), 98 1 (C-1, α), 105 2 (C-1′, α), 109 3, 111 8 [4 C, 3 *C*-$(CH_3)_2$], 127 6, 127 9, 128 0, 128 4, (20 C, 4 phenyl, C-2–6), 138 1 (2 C), 138 2, and 138 8 (4 C, phenyl C-1)

*Methyl 2,3-*O*-isopropylidene-5-*O*-trityl-α,β-*D*-ribofuranoside* (**17**, **18**) — A solution of 2,3-*O*-isopropylidene-5-*O*-trityl-D-ribofuranose* (**16**) (0 48 g, 1 1 mmol), *s*-collidine (0 54 g, 4 5 mmol), and tetrabutylammonium bromide (0 70 g, 2 2 mmol) in dichloromethane (5 5 mL) was added to triflic anhydride (0 60 g, 2 2 mmol), followed, after 5 min, by methanol (1 0 mL) The mixture was kept for 18 h at room temperature, and then processed as described for analogous reactions the product was purified by column chromatography, yield, 0 28 g (59%) of a colorless oil ^{13}C-n m r data δ 25 3 and 26 7 [C(*C*H_3)$_2$, β), 25 8 and 26 1 [C(*C*H_3)$_2$, α], 54 7 (OCH_3, β), 56 3 (OCH_3, α) 64 3 (C-5, β), 64 7 (C-5, γ), 80 8, 81 5, 81 8 (C-2–4, γ), 82 2, 85 3, 86 1 (C-2–4, β), 103 7 (C-1, α) 109 4 (C-1, β), 114 7 [*C*(C_6H_5)$_3$], 127 3, 127 9, 128 7 (15 C, phenyl C-2–6) and 143 6 (3 C phenyl C-1) Based on relative signal-intensities, the ratio of α β (**17** **18**) = 3 2

*Methyl 2,3 5,6-di-*O*-isopropylidene-α- and -β-*D*-mannofuranoside* (**19** *and* **20**) — A solution of crystalline 2 3 5,6-di-*O*-isopropylidene-γ-D-mannofuranose (0 26 g, 1 0 mmol), *s*-collidine (0 36 g, 3 0 mmol) and tetrabutylammonium bromide (0 64 g, 2 0 mmol) in dichloromethane (5 mL) was added to triflic anhydride (0 41 g, 1 5 mmol at −70°, and 15 min later, when t l c showed that all of the aldose had reacted, methanol (1 5 mL) was added The mixture was kept for 18 h, at room temperature and processed as already described Column chromatography (eluant, 9 1 chloroform–ether) afforded two products the first fraction consisted of **19** (0 06 g, 22%), $[\alpha]_D$ +37° (*c* 3, chloroform) (lit [37] $[\alpha]_D$ +50°), the p m r spectrum corresponded closely to that reported[37] for **19** ^{13}C-n m r data δ 24 6, 25 3, 26 0, 26 9 [4 C(*C*H_3)$_2$], 54 6 (OCH_3), 67 0 (C-4), 73 7, 75 7, 80 4 85 1 (C-2,3,5,6), 107 5 (C-1), 109 3, and 112 7 [2 *C*(CH_3)$_2$] The second chromatographic fraction consisted of **20** (0 08 g 30%) $[\alpha]_D$ −37° (*c* 3, chloroform) (lit [38] $[\alpha]_D$ −42°), the p m r spectrum corresponded closely to that reported[37] for **20**, ^{13}C-n m r data δ 25 1, 25 4, 25 7, 27 0 [4 C(*C*H_3)$_2$], 58 0 (OCH_3), 66 9 (C-4), 73 4, 77 3, 79 2, 79 2, 79 7 (C-2,3 5 6) 104 2 (C-1), 109 2, and 115 0 [2 *C*(CH_3)$_2$]

*3,4,6-Tri-*O*-acetyl-1,2-*O*-[1-exo-(2,3 4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyloxy)-ethylidene]-α-*D*-glucopyranose* (**22**) — A solution of crystalline 2,3,4 6-tetra-*O*-acetyl-α-D-glucopyranose (1 4 g, 4 mmol), *s*-collidine (1 45 g, 12 mmol), and triflic anhydride (1 64 g, 6 mmol) in dicnloromethane (20 mL) was kept for 1 h, washed successively

*Prepared as described by Fox *et al* [36], in $CDCl_3$, the oily compound equilibrated to a 5 5 mixture of α and β anomers

with M hydrochloric acid, M sodium hydrogencarbonate, and water, and evaporated, the oily residue was found by t l c to consist of a major and several minor components Column chromatography (eluant, 9 1 chloroform–ether) afforded **22** (0 6 g, 44%), which crystallized in cold methanol, but melted below room temperature, $[\alpha]_D$ +10° (*c* 6, chloroform), M_D +70° [Calc for **22** M_D +32°, based on model compounds ethyl 2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranoside (M_D −85°) and orthoester **26** (M_D +117°), calc for *α* anomer of **22** M_D +613°, based on ethyl 2,3,4,6-tetra-*O*-acetyl-*α*-D-glucopyranoside (M_D +496°) and orthoester **26** (M_D +117°)], p m r data *δ* 1 7 (s, 3 H, CCH_3), ~2 0 (6 s, 21 H, 7 $COCH_3$), 5 9 (d, 1 H, H-1, $J_{1,2}$ 5 0 Hz) ^{13}C-n m r data *δ* 20 6 (7 C, $COCH_3$), 21 9 (CCH_3), 61 7, 63 0 (C-6,6′), 67 1, 68 2, 70 0, 71 1, 72 3, 73 0, 73 3, 75 6 (C-2–5, C-2′–5), 94 6 (C-1, $J_{C\text{-}1-H\text{-}1}$ 184 Hz), 97 1 (C-1′, $J_{C\text{-}1'-H\text{-}1'}$ 162 Hz), 121 2 (CO_3) 168 8, 169 1 169 3, 169 5, 170 2, 170 4, and 170 6 (C=O)

2,3,4,6-Tetra-O-acetyl-α-D-glucopyranosyl bromide (**25**) — The preceding experiment was repeated, except that tetrabutylammonium bromide (0 64 g) was added to the reaction mixture *before* the triflic anhydride (0 41 g) The product was purified by column chromatography (0 20 g from 0 34 g of 2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranose 50% yield), and recrystallized from ether–hexane m p 89 5–90 5°, $[\alpha]_D$ +186° (*c* 6, dichloromethane), indistinguishable from authentic **25** (m p 89–89 5°, $[\alpha]_D$ −206°) by p m r and ^{13}C-n m r spectroscopy

3,4,6-Tri-O-acetyl-1,2-O-(1-ethoxyethylidene)-α-D-glucopyranose (**26**) — When ethanol was added to a reaction mixture prepared as in the preceding paragraph, a chromatographically pure oil was isolated (0 25 g, 66%) According to its p m r spectrum, the product consisted of a 7 1 mixture of *exo* and *endo* diastereoisomers of **26** (relative intensities of CCH_3 signals[10 39] at *δ* 1 7 and 1 5, 7 1) Crystallization afforded the pure *exo* isomer, m p 91–92°, $[\alpha]_D$ +42° (*c*, 3 chloroform), indistinguishable from an authentic specimen (m p 93 5–94 5°, $[\alpha]_D$ +35°) by p m r spectroscopy

Methyl 2,3,4,6-tetra-O-benzyl-α,β-D-glucopyranoside (**10**, **11**) — Methanesulfonic anhydride (0 25 g 1 5 mmol) was added to a solution of **5** (0 27 g, 0 5 mmol), *s*-collidine (0 36 g, 3 0 mmol), and tetrabutylammonium bromide (0 32 g, 1 0 mmol) in dichloromethane (2 5 mL) After 10 min, methanol (0 8 mL, 20 mmol) was added, and 18 h later, the solution was diluted with chloroform, washed successively with M hydrochloric acid, M sodium hydrogencarbonate, and water, and evaporated Column chromatography of the residual oil afforded a product that was virtually indistinguishable (by t l c , and p m r and ^{13}C-n m r spectroscopy) from the mixture of **10** and **11** already described, yield, 0 17 g (61%), based on the relative intensities of the OCH_3 proton and ^{13}C signals, **10** **11** (α β) = 7 3

On repeating this experiment, but *without* the inclusion of tetrabutylammonium bromide, a mixture of **10** and **11** was isolated (yield, 0 24 g, 87%) in the anomeric ratio of α β = 3 2

2,3,4,6-Tetra-O-acetyl-1-O-(methylsulfonyl)-α-D-glucopyranose — Methanesulfonic anhydride (0 25 g, 1 5 mmol) was added to a solution of 2,3,4,6-tetra-*O*-

acetyl-β-D-glucopyranose (0 35 g, 1 0 mmol) and *s*-collidine (0 36 g, 3 0 mmol) in dichloromethane (5 mL) One hour later, chloroform was added, and the solution was successively washed with M hydrochloric acid, M sodium hydrogencarbonate, and water, and evaporated The brown residue was purified by column chromatography, yielding crystals (from ethyl acetate–hexane) (0 31 g, 74%), m p 108–110°, $[\alpha]_D$ +124° (*c* 1, chloroform) (lit [16] m p 112–113°, $[\alpha]_D$ +121°), p m r data δ 2 2 (s, 3 H, SCH_3), 6 0 (d, 1 H, H-1, $J_{1,2}$ 3 Hz), ^{13}C-n m r data δ 20 5 (4 $COCH_3$), 39 4 (SCH_3), 61 6 (C-6). 67 7, 69 2, 70 2 (C-3–5), 96 0 (C-1), 168 6, 170 0, 170 2, and 170 9 (C=O)

*3,4,6-Tri-*O*-acetyl-1,2-*O*-(1-ethoxyethylidene)-α-*D*-glucopyranose* (**26**) — The addition of ethanol (0 14 g, 3 mmol) to a reaction mixture prepared as in the preceding paragraph resulted in the isolation of 0 37 g (98%) of a crystalline product, m p 92–95° According to its p m r spectrum, the product consisted of orthoester **26** (10 parts) admixed with its *endo* diastereoisomer (1 part)

*2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl chloride* (**29**) — Methanesulfonyl chloride (0 12 g, 1 0 mmol) was added to a solution of **5** (0 27 g, 0 5 mmol) and *s*-collidine (0 24 g, 2 0 mmol) in dichloromethane (2 5 mL) After 4 h, when t l c showed that all of the **5** had reacted, chloroform was added, and the solution was washed successively with M hydrochloric acid M sodium hydrogencarbonate and water, and evaporated, the residue was subjected to column chromatography, affording an oil (0 18 g, 63%), $[\alpha]_D$ +69° (*c* 3, chloroform) (lit [40] $[\alpha]_D$ +62°), p m r data δ 6 1 (d, 1 H, H-1, $J_{1,2}$ 4 0 Hz), ^{13}C-n m r data δ 68 0, 73 0 73 6 (2 C), 75 2 75 8, 76 6, 77 0 78 5 80 0, 81 5 (C-2–6, 4 CH_2), 93 5 (C-1, $J_{C\text{-}1,H\text{-}1}$ 180 Hz), 128 1, 128 4, 128 6 (20 C, phenyl C-2–6), 137 7, 137 9, 138 3, and 138 7 (4 C, phenyl C-1)

*2,3 5,6-Di-*O*-isopropylidene-α-D-mannofuranosyl chloride* (**30**) — Under the conditions described for the synthesis of **29**, the reaction of 2 3 5 6-di-*O*-isopropylidene-α-D-mannofuranose (0 26 g, 1 0 mmol) with methanesulfonyl chloride (0 24 g, 2 0 mmol) afforded a chromatographically pure oil (0 20 g, 72%), $[\alpha]_D$ +58° (*c* 9, chloroform) p m r data δ 6 0 (s, 1 H, H-1, $J_{1,2}$ <1 Hz), ^{13}C-n m r data δ 24 7, 25 3, 25 9, 26 9 [$C(CH_3)_2$] 66 9 (C-6) 72 5 78 7 82 6 89 4 (C-2–5), 97 8 (C-1), 109 6 and 113 4 [2 C $C(CH_3)_2$]

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REFERENCES

1 J Leroux and A S Perlin *Carbohydr Res* 47 (1976) c8–c10
2 C P J Glaudemans and H G Fletcher Jr , *Methods Carbohydr Chem* 6 (1972) 373–376
3 M N Preobrazhenskaya and N N Suvorov, *Zh Obshch Khim* 35 (1965) 888–893
4 T Ishikawa and H G Fletcher, Jr *J Org Chem* 34 (1969) 563–571
5 R U Lemieux, K B Hendriks, R V Stick, and K James *J Am Chem Soc* 97 (1975) 4056–4062

6 A J RHIND-TUTT AND C A VERNON, *J Chem Soc*, (1960) 4637–4644
7 R U LEMIEUX AND A R MORGAN, *J Am Chem Soc*, 85 (1963) 1889–1890
8 R J FERRIER, R W HAY, AND N VETHAVIYASAR, *Carbohydr. Res*, 27 (1973) 55–61
9 P A GENT AND R GIGG, *J Chem Soc Perkin Trans 1*, (1974) 1446–1455
10 A S PERLIN, *Can J Chem*, 41 (1963) 399–406
11 A S PERLIN AND B CASU, *Tetrahedron Lett*, (1969) 2821–2924
12 J A SCHWARCZ AND A S PERLIN *Can J Chem*, 50 (1972) 3667–3676
13 M MAZUREK AND A S PERLIN, *Can J Chem*, 43 (1965) 1918–1923
14 H R GOLDSCHMID AND A S PERLIN, *Can J Chem*, 39 (1961) 2025–2034
15 C-S GIAM, H R GOLDSCHMID, AND A S PERLIN, *Can J Chem* 41 (1963) 3074–3080
16 B HELFERICH AND A GNUCHTEL, *Ber*, 71 (1938) 712–718
17 R S TIPSON, *Adv Carbohydr Chem* 8 (1953) 107–215
18 P A J GORIN AND A S PERLIN, *Can J Chem*, 39 (1961) 2474–2485
19 R U LEMIEUX AND J-I HAYAMI *Can J Chem*, 43 (1965) 2162–2173
20 K HESS AND L KINZE, *Ber*, 70 (1937) 1139–1142
21 A COLLEY *C R Acad Sci*, 70 (1870) 401–403
22 K TAKIURA AND S HONDA, *Chem Pharm Bull*, 18 (1970) 2125–2130
23 P DI CESARE AND B GROSS, *Carbohydr Res* 58 (1977) c1–c3
24 B CASTRO Y CHAPLEUR AND B GROSS *Tetrahedron Lett* (1975) 3947–3949
25 F J KRONZER AND C SCHUERCH *Carbohydr Res*, 27 (1973) 379–390, 33 (1974) 273–280
26 T J LUCAS AND C SCHUERCH, *Carbohydr Res*, 39 (1975) 39–45
27 R EBY AND C SCHUERCH *Carbohydr Res*, 50 (1976) 203–214
28 S HANESSIAN AND J BANOUB *Carbohydr Res*, 44 (1975) c14–c17
29 S HANESSIAN AND J BANOUB, *Carbohydr Res*, 53 (1977) c13–c16
30 J LEROUX AND A S PERLIN *Am ACFAS* 41 (1974) 49
31 E FISCHER AND K RASKE, *Ber*, 43 (1910) 1750–1753
32 H OHLE AND K SPENCKER, *Ber*, 59 (1926) 1836–1848
33 L D HALL AND D C MILLER, *Carbohydr Res*, 40 (1975) c1–c2
34 C G BERGSTROM AND S SIEGAL, *J Am Chem Soc*, 74 (1952) 145–152, 254–257
35 H J REICH M JAUTELOT M T MUSSE, F J WEIGERT AND J D ROBERTS, *J Am Chem Soc*, 91 (1976) 7445–7454
36 R S KLEIN, H OHRUI AND J J FOX *J Carbohydr Nucleos Nucleot*, 1 (1974) 265–271
37 M H RANDALL *Carbohydr Res* 11 (1969) 173–178
38 P A LEVENE AND E T STILLER, *J Biol Chem* 102 (1933) 187–201
39 R U LEMIEUX AND A R MORGAN *Can J Chem*, 43 (1965) 2205–2213
40 V. D GROB T G SQUIRES AND J R VERCELLOTTI *Carbohydr Res* 10 (1969) 595–597, P W AUSTIN F E HARDY J G BUCHANAN AND J BADDILEY, *J Chem Soc*, (1964) 2128–2137