tion, washed with ether, and dried over NaOH. The yield was 53.6 g (crude, mp 103–108°) after recrystallization from chloroform–petroleum ether. To a solution of benzoic acid (75 g) in anhydrous ether (600 ml) was added 29.5 g of the *p*-tolyliodine diacetate, and the mixture was stirred for 4 hr. The fine white precipitate was then recrystallized from chloroform–petroleum ether giving 21.5 g, mp 148.5–150.5°. The melting point after a second recrystallization was 149–151°.

Anal. Calcd for $C_{21}H_{17}IO_4$: C, 54.80; H, 3.72; I, 27.58; equiv wt, 230.1. Found: C, 55.00; H, 3.86; I, 27.49; equiv wt, 230.5, 229.3.

Kinetics.—Ampoules were washed with chromic acid, rinsed five times with water, soaked in alkaline phosphate solution, rinsed six times with water and twice with methanol, then dried in an oven. After constricting for sealing they were returned to the oven for storage. Chlorobenzene was shaken with H_2SO_4, then four times with water, twice with aqueous bicarbonate, and again with water. After drying with $MgSO_4$ and $CaCl_2$ it was freshly distilled from P_2O_5 through a column before use. Phenyliodine dibenzoate (stored in a desiccator) and any other solutes required by the run were weighed out and washed into a 100-ml volumetric flask with chlorobenzene. Ampoules were removed from the oven, cooled, and flushed in a stream of N_2, then filled with a 10-ml aliquot by means of an automatic pipet. After an additional flushing with N_2 they were subjected to two or more degassing cycles (freezing, pumping, thawing, freezing) before sealing under vacuum. All of the ampoules of a single run were put in the thermostated bath, and the first, or $t = 0$, ampoule was removed after a 3–5-min warm-up period. The contents of the ampoule was added to 10 ml of acetic acid containing a pellet of CO_2, then 1 ml of saturated KI solution was added, and the flask was lightly stoppered for a few minutes. Finally 10–20 ml of carbonated water was added and the iodine was titrated with sodium thiosulfate.

In some experiments the solid solutes were weighed into each ampoule individually, connected to the vacuum manifold, and filled with solvent by distillation from a bulb containing a large excess of P_2O_5.

Product Analysis.—Free iodine was determined spectrophotometrically. Benzoic acid was determined spectrophotometrically and by isolation. Iodobenzene, chlorobiphenyls, and phenyl benzoate were separated and determined by vapor–liquid partition chromatography over silicone on firebrick, using infrared spectra and the retention times of authentic samples.

Conversion of Equatorial Mesyl Esters of Carbohydrates to Ethers with Retention of Configuration by Reaction with Alkoxides in Dimethyl Sulfoxide[1]

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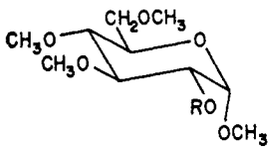
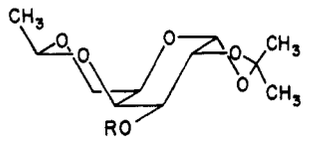
Mesyl esters of equatorial secondary hydroxyl groups in pyranose rings and of a secondary hydroxyl group in a furanose ring reacted readily with sodium methoxide or ethoxide in dry dimethyl sulfoxide. In each case, the products were the corresponding alkyl ether and hydroxy compound, both of which retained the original configuration. Experiments with ^{18}O-labeled sodium methoxide indicated that the alkoxide oxygen was not incorporated into the alkyl ether. The probable reaction mechanism involves an initial slow nucleophilic attack by the alkoxide ion on sulfur in the mesyl ester followed by a rapid competition between the liberated carbohydrate oxide anion and the excess alkoxide for the alkyl mesylate produced.

The remarkable effects of dipolar aprotic solvents on the rate or course of base-catalyzed reactions[3] and our interest in the chemistry of sulfonyl esters of carbohydrates led us to a study of the reactions of some mesyl esters with alkoxides in dimethyl sulfoxide (DMSO). In the present work, the esters were chosen such that the mesyl group was "isolated"; *i.e.*, the other hydroxyl functions were blocked by unreactive and nonparticipating groups.[4] In addition, the mesyl groups in the six-membered ring compounds were in equatorial conformations.

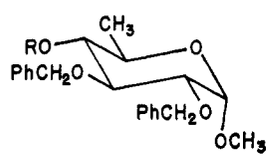
Treatment of methyl 2-*O*-mesyl-3,4,6-tri-*O*-methyl-α-D-glucoside (**1**) with a tenfold excess of sodium methoxide in anhydrous DMSO for 1 hr at 70° gave a mixture of methyl 2,3,4,6-tetra-*O*-methyl-α-D-glucoside (**2**) and methyl 3,4,6-tri-*O*-methyl-α-D-glucoside (**3**). The products were isolated and identified by comparison of physical properties with those of authentic samples and these structures were confirmed by hydrolysis of the methyl tetra-*O*-methylglycoside to crystalline 2,3,4,6-tetra-*O*-methyl-D-glucose and by remesylation of the methyl tri-*O*-methylglycoside to give **1**. Under similar conditions, 4,6-*O*-ethylidene-1,2-*O*-isopropylidene-3-*O*-mesyl-D-galactose (**4**)[5] gave a mixture of 4,6-*O*-ethylidene-1,2-*O*-isopropylidene-3-*O*-methyl-D-galactose (**5**) and 4,6-*O*-ethylidene-1,2-*O*-isopropylidene-D-galactose (**6**). The products were isolated and identified by comparison with authentic compounds and confirmation of the structure of the ether (a syrup) was afforded by mild acid hydrolysis to give crystalline 3-*O*-



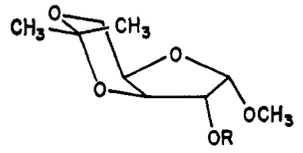
1, R = SO_2CH_3
2, R = CH_3
3, R = H



4, R = SO_2CH_3
5, R = CH_3
6, R = H
7, R = $CH_2{\cdot}CH_3$



8, R = SO_2CH_3
9, R = H
10, R = CH_3



11, R = SO_2CH_3
12, R = H
13, R = CH_3

(1) Preliminary communication, D. H. Ball, E. D. M. Eades, and L. Long, Jr., *J. Am. Chem. Soc.*, **86**, 3579 (1964).

(2) National Academy of Sciences–National Research Council Visiting Scientist, Resident Research Associate.

(3) (a) A. J. Parker, *Quart. Rev.* (London), **16**, 163 (1962); (b) C. A. Kingsbury, *J. Org. Chem.*, **29**, 3262 (1964).

(4) R. S. Tipson, *Advan. Carbohydrate Chem.*, **8**, 107 (1953).

(5) D. H. Ball, *J. Org. Chem.*, **31**, 220 (1966).

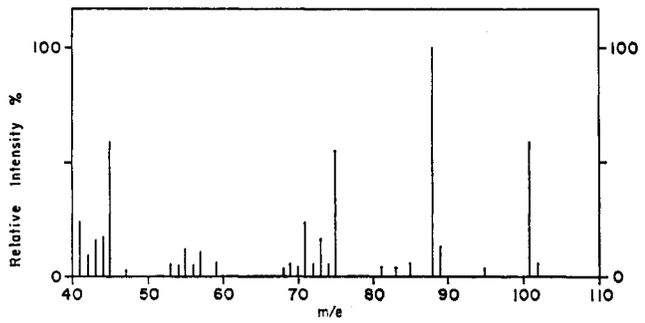


Figure 1.—Mass spectrum of methyl tetra-*O*-methyl-α-D-glucopyranoside formed when **1** was treated with sodium ^{18}O-methoxide in dimethyl sulfoxide.

methyl-D-galactose. Treatment of **4** with sodium ethoxide under the same conditions gave a mixture of **6** and a second product which, from its nmr spectrum, was tentatively identified as the 3-*O*-ethyl derivative of **6**. The specific rotation and infrared and nmr spectra of this compound were found to be identical with those of a sample of 3-*O*-ethyl-4,6-*O*-ethylidene-1,2-*O*-isopropylidene-D-galactose (**7**) prepared by treatment of **6** with ethyl bromide and silver oxide in dimethylformamide. Mild acid hydrolysis of the product and of **7** gave compounds with identical rotations and chromatographic mobilities.

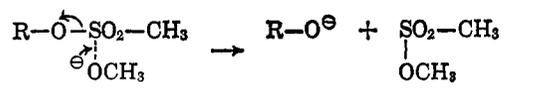
Treatment of methyl 2,3-di-*O*-benzyl-6-deoxy-4-*O*-mesyl-α-D-glucoside (**8**) with sodium methoxide in DMSO as above gave two products: component A, an *O*-methyl ether, and component B, a hydroxyl-containing compound. Treatment of B with mesyl chloride in pyridine gave crystalline starting material (**8**) and methylation of B gave a syrupy product identical with A. Thus, B was methyl 2,3-di-*O*-benzyl-6-deoxy-α-D-glucopyranoside (**9**) and A was methyl 2,3-di-*O*-benzyl-6-deoxy-4-*O*-methyl-α-D-glucoside (**10**).

The three esters **1**, **4**, and **8**, having equatorial mesyloxy groups at the 2, 3, and 4 positions, respectively, in the pyranose ring, gave similar reactions resulting in mixtures of ether and hydroxyl compounds with the original configurations. The mesyloxy group attached to the five-membered ring in methyl 3,5-*O*-isopropylidene-2-*O*-mesyl-α-D-xylofuranoside (**11**) reacted in an analogous way to give methyl 3,5-*O*-isopropylidene-α-D-xylofuranoside (**12**) and the 2-*O*-methyl ether **13**. Compounds **11** and **12**, previously reported as syrups,[6] were obtained crystalline, the latter by preparative gas chromatography.[7]

Preliminary experiments using **1** as substrate were carried out with the aid of thin layer chromatography (tlc) to determine the optimum conditions for the reaction. During these experiments, it was noted that increasing the methoxide concentration or raising the temperature caused an increase in the over-all rate of reaction, but neither factor appeared to affect the relative amounts of the two products. An attempt was made to estimate quantitatively the ratio of ether to alcohol produced at varying concentrations of **1** by vapor phase chromatography (vpc).[8] Direct injection of the reaction mixture was unsuccessful since the peak due to **2** could not be completely separated from the large DMSO peak. Accordingly, the reaction mixtures were diluted with water and extracted with chloroform. The extracts were concentrated and examined by vpc, and the peak areas for the ether and alcohol were in the approximate ratio 1.4:1. No significant variation was detected but the results may be imprecise owing to variations in the efficiency of the chloroform extractions of **2** and **3** from water–DMSO mixtures.

Saponifications of "isolated" carbohydrate secondary sulfonate esters usually proceed with difficulty and by O–S cleavage to give the alcohol with retention of configuration (pp 167–170 in ref 4). The mechanism of such reactions is believed to involve a nucleophilic displacement on sulfur in compounds whose stereochemistry makes attack on carbon unfavorable.[9] There appears to have been no previous report of reaction of an "isolated" secondary sulfonate ester with alkoxide to give an ether with the same configuration.

To ascertain whether or not the C–O bond of the ester was broken during the reaction, **1** was treated with sodium ^{18}O-methoxide as above and a pure sample of the methyl tetra-*O*-methyl-α-D-glucopyranoside fraction was isolated. Comparison of its mass spectrum (Figure 1) with that of unlabeled **2** showed that they were identical. Kochetkov and co-workers[10] have analyzed the mass spectrum of **2** by deuteration studies and have estimated the contributions made to individual mass peaks by isomeric ion fragments arising from different parts of the molecule. This work predicts that ions containing the C-2 OCH_3 group account for about 86% of the peak at *m/e* 101 and about 84% of the peak at *m/e* 88. As these are two of the larger peaks in the spectrum (Figure 1), incorporation of $^{18}OCH_3$ at C-2 should be readily detected by the appearance of peaks at *m/e* 103 and *m/e* 90. These peaks were absent from the spectrum indicating that the C-2–O bond of the mesylate was not broken during the reaction. Thus, the alkyl group, but not the ether oxygen, originates in the alkoxide ion and the initial and rate-determining step in the reaction is a nucleophilic attack by methoxide on the sulfur atom of the mesyloxy group.



Addition of 1 equiv of methyl mesylate to a solution of **1** in DMSO at 70° followed by addition of 10 equiv of sodium methoxide did not affect the final ratio of products. The over-all reaction rate was lowered and it appeared that the added methyl mesylate was rapidly destroyed by the methoxide. Thus, as might be anticipated, the rate of attack of methoxide on carbon in methyl mesylate is much greater than the rate of attack of methoxide on sulfur in the carbohydrate mesyl ester.

In an additional experiment,[11] 1 equiv of methyl mesylate was added to a mixture of **3** and 10 equiv of sodium methoxide in DMSO at 70°. A mix-

(6) (a) E. E. Percival and R. Zobrist, *J. Chem. Soc.*, 4306 (1952); (b) B. R. Baker, R. E. Schaub, and J. H. Williams, *J. Am. Chem. Soc.*, **77**, 7 (1955); (c) J. M. Anderson and E. E. Percival, *J. Chem. Soc.*, 819 (1956).

(7) Mesylation of anomerically pure methyl 3,5-*O*-isopropylidene-β-D-xylofuranoside afforded the 2-*O*-mesyl ester which also crystallized and had mp 61–63°, $[\alpha]^{25}D$ −58° (*c* 2.8, chloroform).

(8) Preliminary experiments indicated that a column (10 ft × 0.25 in.) of Apiezon L, 10% on hexamethyldisilazane-treated Chromosorb W, 60–80 mesh, gave a satisfactory separation of **2** from **3** and from DMSO.

(9) C. A. Bunton and Y. F. Frei, *J. Chem. Soc.*, 1872 (1951).

(10) N. K. Kochetkov, N. S. Wulfson, O. S. Chizhov, and B. M. Zolotarev, *Tetrahedron*, **19**, 2209 (1963).

(11) J. C. P. Schwarz, private communication.

ture of **3** and the methyl ether **2** was rapidly formed and addition of a second equivalent of methyl mesylate resulted in further methylation of **3** to give **2**.

It appears then that the second stage of the reaction involves a competition between methoxide and the carbohydrate anion for the methyl mesylate formed in the first stage. In view of the large excess of methoxide usually employed and the apparent insensitivity of the product ratio to changes in methoxide concentration, it would seem that the carbohydrate oxide anion is a much stronger nucleophile toward carbon than is methoxide in DMSO. The methyl mesylate and the carbohydrate anion are produced simultaneously and, since the first stage of the reaction is slow compared with the second stage, the concentration of the carbohydrate anion at any instant will be small compared with the methoxide concentration. In order to achieve the observed product ratio, the carbohydrate anion must be able to compete with methoxide even at very low relative concentrations. This indicates that the second stage of the reaction takes place before the methyl mesylate can diffuse away from the carbohydrate anion. In effect, this is a "solvent cage" hypothesis of which the four-center intermediate, previously proposed,[1] may be considered an extreme state.

Experimental Section[12]

Reaction of Methyl 2-*O*-Mesyl-3,4,6-tri-*O*-methyl-α-D-glucoside (1) with Sodium Methoxide in DMSO.—To a solution of **1** (1.6 g, 5 mmoles) in DMSO[13] (160 ml) was added dry powdered sodium methoxide (2.7 g, 50 mmoles), and the mixture was stirred at 70°. Tlc (ether) indicated that no starting material remained after 1 hr and that two products were formed, both slower moving than **1**. The reaction mixture was poured into water and the aqueous solution was extracted continuously with ether. Concentration of the dried ($CaSO_4$) ether extract gave an oily residue (containing DMSO) which was fractionated on a column of silica gel (200 g) with ether as eluent to give the two products following.

Component A (0.33 g), the faster moving product, was indistinguishable from methyl 2,3,4,6-tetra-*O*-methyl-α-D-glucoside (**2**) by infrared and nmr spectroscopy and by vpc on Apiezon L at 177°. (Under the conditions used, methyl 2,3,4,6-tetra-*O*-methyl-α-D-mannoside had R_v 0.86 relative to **2**.) A portion of A (0.25 g) was hydrolyzed with 2 *N* hydrochloric acid at 100° for 3 hr. The solution was neutralized [Amberlite IR 45 (OH^-)] and concentrated to a syrup which crystallized. Recrystallization from petroleum ether (bp 60–110°) gave colorless needles (0.17 g) with mp 94–96°, not depressed by admixture with authentic 2,3,4,6-tetra-*O*-methyl-α-D-glucose. The infrared spectra of the hydrolysis product and of 2,3,4,6-tetra-*O*-methyl-α-D-glucose were identical.

Component B (0.22 g) was indistinguishable from methyl 3,4,6-tri-*O*-methyl-α-D-glucoside (**3**) by infrared and nmr spectroscopy. A portion of B (0.2 g) was treated with mesyl chloride (0.1 g) in pyridine (3 ml). After 8 hr at 0°, the solution was allowed to come to room temperature and was then concentrated to a solid residue which was taken up in an ethanol–toluene mixture and reconcentrated to remove most of the pyridine. The residue was extracted with ether; the extracts were treated with charcoal and reconcentrated to a syrup which crystallized. Recrystallization from ether–heptane gave colorless crystals with mp 90.5–91.5°,[14] not depressed by admixture with authentic methyl 2-*O*-mesyl-3,4,6-tri-*O*-methyl-α-D-glucoside (**1**). The infrared and nmr spectra of the product and of **1** were identical.

Reaction of 4,6-*O*-Ethylidene-1,2-*O*-isopropylidene-3-*O*-mesyl-D-galactose (4) with Sodium Methoxide in DMSO.—To a solution of **4** (0.90 g, 2.8 mmoles) in DMSO (90 ml) was added sodium methoxide (1.5 g, 28 mmoles) and the solution was stirred at 70°. After 1 hr, tlc (ether) indicated the absence of starting material and the formation of two products. Water (300 ml) was added and the solution was deionized by passage down a column of Amberlite MB 1 resin. The aqueous effluent was concentrated to an oily residue (containing DMSO) which was fractionated on a column of silica gel (200 g) with ether as eluent to give the two components following.

Component A (0.23 g), the faster moving product, had $[\alpha]^{25}D$ +34.5° (*c* 1.5, chloroform) and contained no hydroxyl groups (infrared spectrum in chloroform). The nmr spectrum indicated the presence of the ethylidene and isopropylidene groups and of a methoxyl group (τ 6.49). A solution of A (0.21 g) in 1 *N* hydrochloric acid was heated at 100° for 1 hr, then cooled, neutralized [Amberlite IR 45 (OH^-)], and concentrated to a syrup (0.12 g) which crystallized. Recrystallization from ethanol gave colorless crystals with mp 139–142°, not depressed by admixture with authentic 3-*O*-methyl-α-D-galactose and $[\alpha]^{25}D$ +143 (10 min) → +109° (6 hr, constant, *c* 0.91, water), in good agreement with values previously reported.[15] The infrared spectra and chromatographic mobilities of the product and of 3-*O*-methyl-α-D-galactose were identical. Methylation of 4,6-*O*-ethylidene-1,2-*O*-isopropylidene-D-galactose (**6**) gave 4,6-*O*-ethylidene-1,2-*O*-isopropylidene-3-*O*-methyl-D-galactose (**5**) which was found to be identical with component A (infrared and nmr spectra).

Component B (0.20 g) had $[\alpha]^{25}D$ +56° (*c* 2.1, chloroform) and was indistinguishable from **6** by infrared and nmr spectroscopy. A portion of B (0.18 g) was mesylated as described above for **3** and the product (0.15 g), after recrystallization from ethanol, had mp 98–99°, not depressed by admixture with **4**. The infrared and nmr spectra of the product and of **4** were identical.

Reaction of 4 with Sodium Ethoxide in DMSO.—To a solution of **4** (1.0 g, 3.1 mmoles) in DMSO (100 ml) was added dry powdered sodium ethoxide (2.1 g, 31 mmoles) and the solution was stirred at 70°. Tlc (ether) indicated that reaction was complete after 1 hr and that two products were formed. The reaction mixture was diluted with water (300 ml) and the solution was deionized by passage down a column of Amberlite MB 1 resin. The aqueous effluent was concentrated to an oily residue which was fractionated on a column of silica gel (300 g) with ether as eluent. Two products were obtained.

Component A (0.16 g), the faster moving product, was a pale yellow syrup with $[\alpha]^{25}D$ +18.4° (*c* 7.8, carbon tetrachloride). The infrared spectrum in carbon tetrachloride indicated the absence of any hydroxyl groups and the nmr spectrum was consistent with that expected for a 3-*O*-ethyl derivative of **6**. A portion of **6** (0.20 g) was treated with ethyl bromide (3 ml) and silver oxide (2.5 g) in dimethylformamide (10 ml) at room temperature. The mixture was shaken overnight in the absence of light and then worked up as for a methylation. After purification by chromatography on silica gel with ether as eluent, 3-*O*-ethyl-4,6-*O*-ethylidene-1,2-*O*-isopropylidene-D-galactose (**7**, 0.18 g) had $[\alpha]^{25}D$ +20.5° (*c* 9.2, carbon tetrachloride). The infrared and nmr spectra of **7** and of component A were identical and acid hydrolysis of each gave syrupy products (3-*O*-ethyl-D-galactose) with the same rate of movement on paper chromatograms.

Component B (0.17 g) was identified as **6** by comparison of its infrared and nmr spectra with those of authentic material.

Reaction of Methyl 2,3-Di-*O*-benzyl-6-deoxy-4-*O*-mesyl-α-D-glucoside (8) with Sodium Methoxide in DMSO.—To a solution of **8** (1.45 g, 0.3 mmole) in DMSO (100 ml) was added dry powdered sodium methoxide (1.62 g, 3.0 mmoles) and the mixture was stirred at 65°. Tlc (isopropyl ether) indicated complete removal of **8** in 1 hr and the formation of two products. The mixture was poured into water (300 ml) and the aqueous solution was extracted continuously with ether for 20 hr. Concentration of the dried (sodium sulfate) ether extract afforded a

(12) Infrared spectra were recorded on a Perkin-Elmer Infracord spectrophotometer and the nmr spectra were recorded on a Varian Model A-60 spectrometer. Melting points were determined on a Thomas–Hoover capillary melting point apparatus and optical rotations were measured with an ETL-NPL automatic polarimeter (The Bendix Corp., Cincinnati, Ohio). Ascending tlc was performed on 0.25-mm layers of silica gel G (distributed by Brinkmann Instruments, Inc., Great Neck, N. Y.) and the plates were sprayed successively with a 1% solution of α-naphthol in ethanol and with 10% sulfuric acid and were then heated. Silica gel, grade 950, 60–200 mesh, from the Davison Co., Baltimore, Md., was used without pretreatment for column chromatography. Vpc was carried out using a Perkin-Elmer vapor fractometer, Model 154. Solvents were removed under reduced pressure. The authors wish to thank Mr. C. DiPietro for the microanalyses.

(13) DMSO was dried and distilled over Linde 13X Molecular Sieves.

(14) A. K. Mitra, D. H. Ball, and L. Long, Jr., *J. Org. Chem.*, **27**, 160 (1962).

(15) F. Reber and T. Reichstein, *Helv. Chim. Acta*, **28**, 1164 (1945).

syrupy residue which was fractionated on a column of silica gel (140 g) with isopropyl ether as eluent to give the two following products.

Component A (0.40 g), the faster moving product, had $[\alpha]^{25}D$ +74.6° (*c* 5.2, carbon tetrachloride) and was shown to be methyl 2,3-di-*O*-benzyl-6-deoxy-4-*O*-methyl-α-D-glucoside (**10**) by comparison of its infrared and nmr spectra with those of an authentic sample of **10** (see below).

Component B (0.44 g) had $[\alpha]^{25}D$ +32.5° (*c* 5.3, carbon tetrachloride) and showed hydroxyl absorption in the infrared. The nmr spectrum was consistent with that anticipated for methyl 2,3-di-*O*-benzyl-6-deoxy-α-D-glucopyranoside (**9**). A portion of B (0.15 g) was treated with mesyl chloride in pyridine as described above for **3** and the product, after recrystallization from ethanol, had mp 110–110.5°, not depressed by admixture with authentic **8**. The infrared and nmr spectra of the product and of **8** were identical.

A portion of B (0.15 g) was methylated by the Kuhn procedure and the syrupy product was distilled at 0.1 mm (bath temperature 150°) to give pure methyl 2,3-di-*O*-benzyl-6-deoxy-4-*O*-methyl-α-D-glucoside (**10**) with $[\alpha]^{25}D$ +75° (*c* 5.3, carbon tetrachloride).

Anal. Calcd for $C_{22}H_{28}O_5$: C, 70.94; H, 7.58. Found: C, 71.08; H, 7.64.

Preparation of Pure Methyl 3,5-*O*-Isopropylidene-α-D-xylofuranoside (12) and Its Crystalline 2-*O*-Mesyl Derivative (11).—A suspension of D-xylose (50 g) in methanol (1 l.) containing concentrated hydrochloric acid (10 ml) was stirred for 5 hr. The solution was neutralized by passage down a column of Dowex 3 (OH^-) and concentrated to a syrup (56 g). Tlc in all solvents tried did not separate the two furanosides. The syrup was taken up in acetone (500 ml), anhydrous cupric sulfate (100 g), and 1 *N* sulfuric acid (1 ml) were added, and the suspension was shaken overnight (17 hr). The mixture was then filtered and the filtrate was neutralized with ammonia and concentrated to a syrup. This was taken up in water (50 ml) and the aqueous solution was extracted with chloroform (three 50-ml portions). The extracts were dried (magnesium sulfate), concentrated, and distilled. The distillate was diluted with an equal volume of acetone and separated into the α and β anomers of methyl 3,5-*O*-isopropylidene-D-xylofuranoside by preparative vpc. The instrument used was a Wilkens Autoprep (Model A-700) equipped with a 5 ft × 3/8 in. column of Carbowax 20M, 30% on Chromosorb P (60–80 mesh). The separation was effected at a column temperature of 225° and a flow rate of 200 cc of nitrogen/min and the solution was injected in 0.5-ml portions. The two anomers were redistilled and the α form crystallized when stored at −10°. It had mp 16–17° and $[\alpha]^{25}D$ +76° (*c* 3.9, water) and +90° (*c* 2.9, chloroform).

Anal. Calcd for $C_9H_{16}O_5$: C, 52.93; H, 7.90. Found: C, 52.76; H, 8.00.

The nmr spectrum (in deuteriochloroform solution) showed a doublet for the anomeric proton at τ 4.80 with $J_{1,2}$ = 4 cps and the C-2 hydroxyl proton appeared as a sharp doublet at τ 7.00 with J = 3.5 cps.

To a solution of the α anomer (4.0 g) in dry pyridine (10 ml) at 0° was added mesyl chloride (1.6 ml, 1.1 equiv). The solution was allowed to come to room temperature and tlc (ether) indicated complete mesylation after 2 hr. The mixture was diluted with methylene chloride and filtered to remove pyridine hydrochloride. Concentration of the filtrate afforded a syrup which was purified by chromatography on a composite column of Alumina (Woelm, neutral, activity grade I, 100 g) over silica gel (200 g) with ether as eluent. The product crystallized from ether–hexane and recrystallization from ethanol afforded pure methyl 3,5-*O*-isopropylidene-2-*O*-mesyl-α-D-xylofuranoside (**11**, 4.7 g, 84%) with mp 54–55°, $[\alpha]^{25}D$ +100° (*c* 1.8, chloroform).

Anal. Calcd for $C_{10}H_{18}O_7S$: C, 42.54; H, 6.43; S, 11.36. Found: C, 42.33; H, 6.52; S, 11.46.

Reaction of 11 with Sodium Methoxide in DMSO.—To a solution of **11** (1.4 g, 5 mmoles) in DMSO (170 ml) was added sodium methoxide (2.7 g, 50 mmoles) and the solution was stirred at 65°. Tlc (ether) indicated complete removal of starting material after 1 hr. The cooled reaction mixture was poured into water (500 ml), deionized by passage down a column of Amberlite MB-1 resin, and concentrated to an oily residue (*ca.* 1 g). Fractionation of this residue on a column of silica gel (130 g) with ether as eluent gave only a partial separation: the two components were obtained pure together with a fraction containing both products.

Component A (80 mg), the faster moving product, had $[\alpha]^{25}D$ +88° (*c* 1.8, carbon tetrachloride) and was identified as methyl 3,5-*O*-isopropylidene-2-*O*-methyl-α-D-xylofuranoside (**13**) by comparison of its retention volume on vpc (Carbowax 1500 at 198°) and its infrared and nmr spectra with those of authentic material. Acid hydrolysis of a portion of A gave a product indistinguishable from authentic 2-*O*-methyl-D-xylose on paper chromatograms.

Component B (150 mg) was identified as **12** by comparison of its infrared and nmr spectra with those of authentic material.

Preparation of Sodium ^{18}O-Methoxide.—To ether-washed "bird-shot" sodium[16] (0.5 g, weighed in an atmosphere of dry nitrogen) in anhydrous ether (30 ml) were added ^{18}O-methanol (500 mg, 55.5% ^{18}O) and unlabeled methanol (300 mg) and the mixture was boiled under reflux for 18 hr with protecting tubes of calcium chloride and soda lime. The ether was removed by blowing dry nitrogen through the system and excess methanol was removed by storage *in vacuo* over calcium chloride for 4 hr to give a white powder (1.15 g).

Reaction of 1 with Sodium ^{18}O-Methoxide in DMSO.—A solution of **1** (0.8 g) in DMSO (80 ml) at 70° was treated with sodium ^{18}O-methoxide (1.15 g) and the methyl tetra-*O*-methyl-D-glucopyranoside fraction (0.26 g) was isolated as previously described. It had $[\alpha]^{25}D$ +146° (*c* 3.7, chloroform) and was indistinguishable from authentic **2** by vpc and by infrared spectroscopy. The mass spectrum of the product[17] was identical with that of **2** (Figure 1).

Preparation of Methyl Mesylate.[18]—To a stirred solution of methanesulfonic acid (25 g, 0.26 mole) in dry acetonitrile (250 ml) at 0° was slowly added silver oxide (62 g, 0.27 mole) during 1 hr. The mixture was then heated to boiling, cooled, and filtered to remove unreacted silver oxide and the filtrate was concentrated to a solid residue of silver mesylate (52 g) which was dried *in vacuo* over silica gel. To a stirred solution of silver mesylate (25 g) in dry acetonitrile (130 ml) at room temperature was added methyl iodide (20 g). Silver iodide precipitated and after 15 min was removed by filtration. The filtrate was concentrated to a syrup which was distilled: bp 86–90° (12 mm), yield 6 g, $n^{25}D$ 1.4131.[19]

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(16) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1955, p 341.

(17) The authors wish to thank Mr. M. L. Bazinet for the mass spectra which were recorded with a Consolidated Electrodynamics Corp., Model 21-103C, mass spectrometer.

(18) W. D. Emmons and A. F. Ferris, *J. Am. Chem. Soc.*, **75**, 2257 (1953).

(19) W. E. Bissinger, F. E. King, and C. W. Hamilton [*ibid.*, **70**, 3940 (1948)] report $n^{20}D$ 1.4140, bp 100.5–101.5° (25 mm).