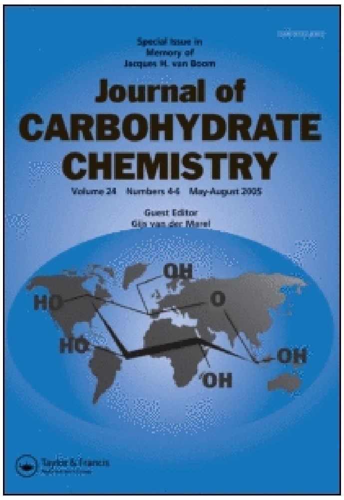

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Photolysis of Methylsulfonyl and Benzyl Protected Carbohydrates

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PHOTOLYSIS OF METHYLSULFONYL AND BENZYL PROTECTED CARBOHYDRATES[1]

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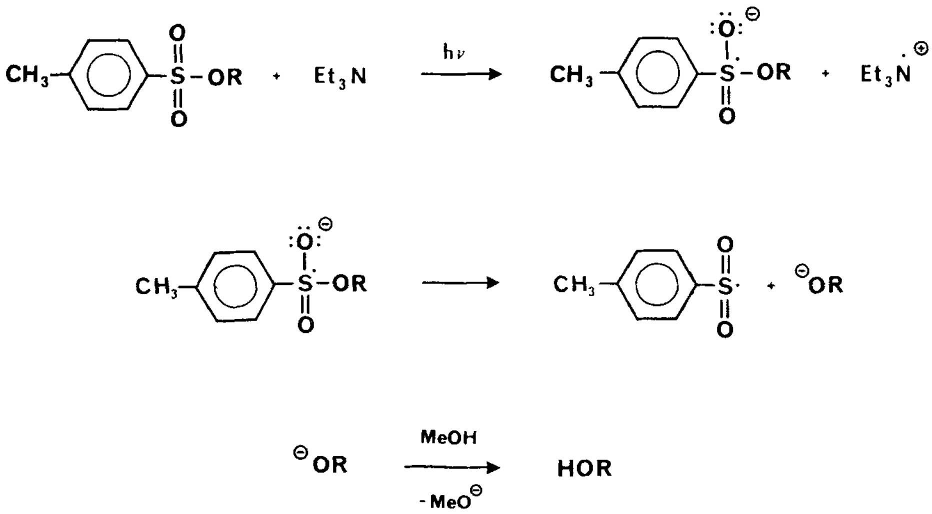
ABSTRACT

The methanesulfonates **1-6**, which are protected by cyclic or acyclic acetals, were irradiated in methanol, containing potassium iodide, with 254 nm UV light. In each case photolysis caused the replacement of the methylsulfonyl group with hydrogen. When an acetyl, benzoyl, *p*-tolylsulfonyl, or benzyl group was present (compounds **13**, **14**, **15**, and **16**, respectively), irradiation caused removal of these groups in preference to the methyl sulfonyl group. Additional study of the benzyl protected compounds **17-19** showed that irradiation in the presence of iodide ion is an effective method for debenzylation.

INTRODUCTION

Since photochemical reactions are normally conducted at room temperature and often in the absence of acidic or basic catalysts, photoremovable protecting groups can have a significant advantage over their non-photochemical counterparts in situations where deprotection needs to be conducted under mild conditions. Among the photolabile groups in common use in carbohydrate synthesis, the *p*-tolylsulfonyl group has enjoyed wide application.[2] *p*-Tolylsulfonyl protection has been used in a number of situations even though the strongly basic sodium hydroxide is typically added to reaction mixtures

Scheme I



during deprotection.[2,3] (Product yields decrease when hydroxide ion is omitted.) Recent mechanistic studies have shown that the number and type of situations in which *p*-tolylsulfonyl protection is possible can be dramatically increased by replacing hydroxide ion in the reaction mixture with a much less basic tertiary amine. These mechanistic studies demonstrated that amines promote the photochemical reaction by functioning as electron donors.[4] By providing the excited *p*-tolylsulfonyl group with an electron, the amine participates in formation of a radical anion that then fragments to give the deprotected sugar (Scheme I, R = sugar residue).

One question raised by *p*-tolylsulfonyl photoreaction concerns the ability of other sulfonate esters to experience similar processes. Due to their widespread use in carbohydrate synthesis, it is of particular interest to determine whether methanesulfonates, which do not absorb UV light effectively except at very short wavelengths, also can experience photochemical deprotection. Interest in making this determination prompted the investigation described here.

RESULTS AND DISCUSSION

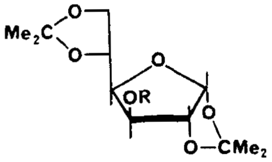
Our attention focused initially on the methanesulfonates **1-6**. The first experiment conducted was irradiation of 1,2:5,6-di-*O*-isopropylidene-3-*O*-methylsulfonyl-α-**D**-glucofuranose (**1**) under conditions (in methanol in the presence of triethylamine with 254 nm incident light) in which the corresponding *p*-toluenesulfonate experienced deprotection.[4] Photolysis of the methanesulfonate **1** produced no reaction. This result was not surprising since compound **1** has very little UV absorption at 254 nm; however, even when shorter wavelength light was employed, no significant reaction was observed. These results determined that if photochemical deprotection of methanesulfonates was to occur, a basically different approach had to be taken.

The strategy adopted was one suggested by the work of Jortner and coworkers[5] who observed that irradiation of halide ions caused electron ejection into solution to generate solvated electrons and the corresponding halogen atoms. If an ejected electron were captured by a methylsulfonyl group, the radical anion produced would be analogous to that formed from *p*-toluenesulfonate photolysis (Scheme I, R = sugar residue).[4] Furthermore, if such a process did occur, fragmentation of the radical anion leading to the deprotected sugar then would be expected to ensue. When the methanesulfonate **1** was dissolved in methanol and irradiated in the presence of potassium iodide, deprotection took place to give **7** in 90% yield. The methanesulfonates **2-6** (Table I) experienced similar photochemical reaction under these conditions to give compounds **8-12**, respectively.

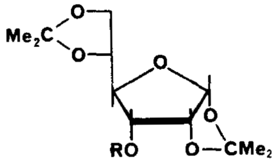
None of the compounds **1-6** contained chromophores that would prevent iodide ion from absorbing the incident light nor did these compounds have electronegative groups which could compete with the methylsulfonyl group for capture of an electron. Since a number of common protecting groups, however, do possess such chromophores and electronegative groups, compounds **13-16**, containing such protecting groups,

TABLE I

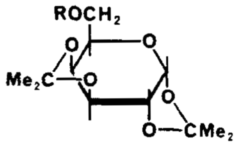
$$R'OR \xrightarrow[\text{MeOH}\ \ NaHCO_3]{h\nu\ \ \text{KI}} R'OH$$



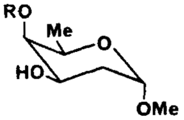
1 R = Ms
90 %
7 R = H
85 %
17 R = Bzl



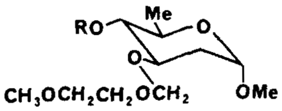
2 R = Ms
61 %
8 R = H
65 %
18 R = Bzl



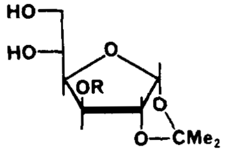
3 R = Ms
64 %
9 R = H
82 %
19 R = Bzl



4 R = Ms
74 %
10 R = H

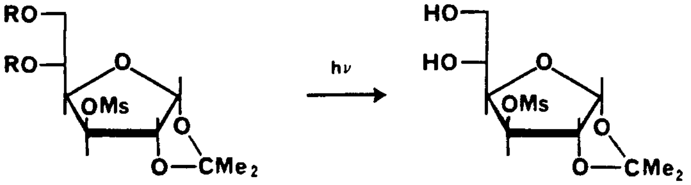


5 R = Ms
70 %
11 R = H



6 R = Ms
60 %
12 R = H

were chosen for additional study. In each case deprotection occurred but for none of these compounds did reaction involve the methylsulfonyl group (eq. 1). Photolysis of **13-16** thus helped to define the situations in which methylsulfonyl protection could be removed without effecting other protecting groups by demonstrating that loss of protecting groups con-



(eq. 1)

13 R = Ac 85 %

14 R = Bz 100 %

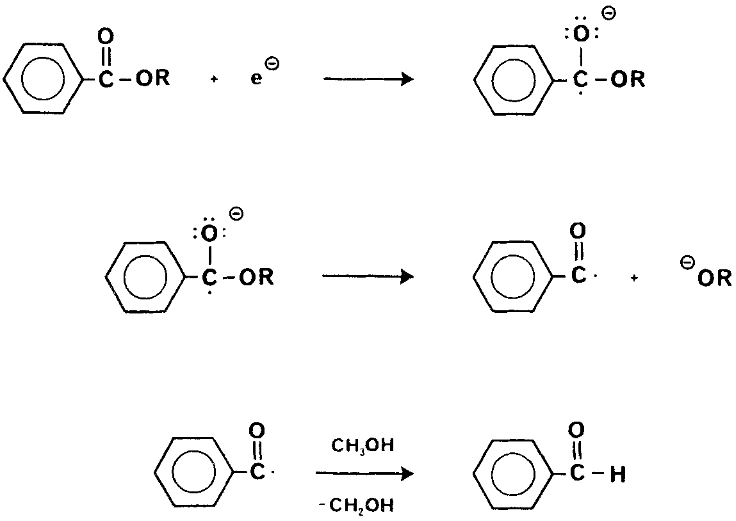
16 R = Bzl 60 %

15 R = Ts 100 %

taining unsaturation (C=C or C=O) occurred in preference to methylsulfonyl deprotection.

With respect to the acylated compounds **13** and **14**, the deprotection process could have been photochemically promoted or it could have been a transesterification occurring under the reaction conditions. To determine if deprotection was the result of a photochemical process, it was necessary to conduct two control reactions. Somewhat surprisingly, the outcome from these reactions was different. Compound **13** experienced essentially complete acetyl deprotection when subjected to the reaction conditions in the absence of light; in contrast, there was only a small amount of solvolysis of the benzoate **14** under these same conditions. Therefore, benzoate deprotection was, at least in part, photochemically promoted. A proposed mechanism for this photochemical process is shown in Scheme II (R = sugar residue). This mechanism is supported by studies in non-carbohydrate systems which have shown that benzoate esters are effective electron acceptors.[6,7] Inherent in this mechanism is the prediction that benzaldehyde should be one of the products of the photochemical process. (Non-photochemical

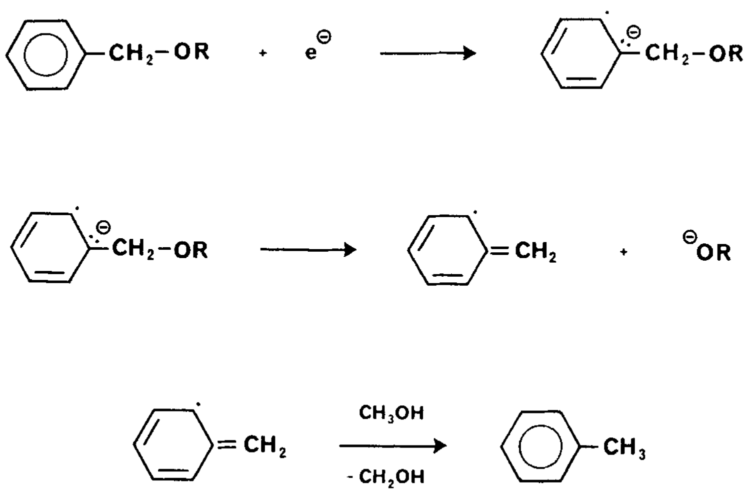
Scheme II



deprotection would produce methyl benzoate.) Since both benzaldehyde and methyl benzoate were present in the reaction mixture after irradiation, it can be concluded that at least part of the deprotection of benzoates results from a photochemical process.[8] (Irradiation of **14** in the absence of potassium iodide did not produce benzaldehyde.)

Benzyl group removal from compound **16** during photolysis in the presence of iodide ion raised questions concerning how this process took place and whether similar reaction would accompany irradiation of other benzyl ethers. Certainly the possibility existed that a radical anion intermediate was involved in this reaction too. A proposed mechanism for such a process is given in Scheme III (R = sugar residue). One test that can be applied to this mechanism is that it predicts that toluene should be formed during photolysis. Since toluene was present in the photolysis mixture from the benzyl ether **16**, we believe that electron transfer is involved in this reaction. The observations that iodide ion is essential to the reaction and that no aromatic products (e.g., benzyl

Scheme III



iodide, benzaldehyde) other than toluene were formed further supports a process such as that outlined in Scheme III.

Finally, since we were interested in determining whether photochemical deprotection would occur when other benzyl ethers were irradiated, photolysis of compounds **17-19** (structures in Table I) in methanol in the presence of potassium iodide was undertaken. Complete deprotection took place to give compounds **7**, **8**, and **9**, respectively. We conclude from irradiation of compounds **17-19** that photochemical debenzylation can be expected when benzyl ethers are irradiated in the presence of electron donors as effective as iodide ion.

EXPERIMENTAL

General Procedures. Column chromatography was conducted using a 2.5 x 15 cm column of 240-400 mesh silica gel (Baker) developed with 1:3 ethyl acetate - hexane, unless otherwise noted. TLC was done using Whatmann silica gel 60A plates developed with 1:3 ethyl acetate - hexane. NMR spectra were determined using a Brucker AC300F spectrometer with deuterochloroform as the solvent. Chemical shifts are relative to tetramethylsilane (δ = 0.0). Mass spectra were obtained using a Finnigan TSQ-45 mass spectrometer. Optical rotations were determined at 578 nm for solutions in ethyl acetate at 22 ^{0}C using a Perkin-Elmer model 241 spectrometer.

General Procedure for Preparation of Methanesulfonates. The partially protected sugar (19 mmol) was dissolved in 11 mL of pyridine. To this stirred solution was added methanesulfonyl chloride (45 mmol). After standing at room temperature for 6 h, the reaction mixture was added slowly to a stirred solution of 50 mL of saturated sodium bicarbonate. The material which separated was collected by filtration (if a solid) or by extraction with 3 x 25 mL of dichloromethane. After evaporation of the solvent under reduced pressure, the remaining material was chromatographed as described in the general procedures.

Methanesulfonates **1**, **2**, **3**, and **15** are known compounds and were identical to compounds prepared as described in references 9, 10, 11, and 12, respectively. The synthesis of the remaining methanesulfonates is described below.

Preparation of Benzyl Ethers 17-19. The benzyl ethers **17**, **18**, and **19** are known compounds and were prepared according to procedures described in references 13, 14, and 15, respectively.

General Photolysis Procedure. Photochemical reactions were conducted in a quartz vessel (5 x 25 cm) using a Rayonet Srinivasan-Griffin apparatus equipped with 16 Rayonet RPR-2537A UV lamps. All photochemical reaction mixtures were purged with nitrogen for 1 h prior to photolysis and the purge was continued during irradiation. The temperature of the reaction mixture was maintained at 17 ^{0}C by use of a water-cooled cold finger. In each case the photochemical reaction mixture consisted of the sugar to be irradiated, 0.5 g of potassium iodide, and 0.5 g of sodium bicarbonate dissolved in 250 mL of methanol. After irradiation, the solvent was evaporated under reduced pressure and the residue was chromatographed as described in the general procedures to give the products shown in eq. 1 and Table I in the yields indicated. The distillate obtained from evaporation of the reaction solvent from compound **14** showed UV absorption suggesting the presence of an aromatic compound. GC/MS analysis of this solvent showed two aromatic compounds. The first had a retention time and mass spectrum identical to benzaldehyde while the second was identical to methyl benzoate. The distillate from evaporation of the irradiation solvent from compound **16** was analyzed in a similar fashion and found to contain toluene.

Control Experiments. Control experiments were conducted on compounds **1**, **13**, **14**, and **16**. For compounds **1** and **16** these experiments consisted of irradiation under the standard conditions except without iodide ion being present. No reaction at all occurred for compound **1** under these conditions. For compound **16** there was a small (5%) decrease in starting material recovered but no deprotection took place to give **6**. For compounds **13** and **14** the control experiments consisted of subjecting the reactants to the standard reaction conditions but wrapping the reaction vessel with aluminum foil to prevent any light from reaching the reaction mixture. Compound **13** experienced complete solvolysis under these conditions to give compound **6** (100%). Compound **14** was more stable and experienced only 15% formation of **6**.

Methyl 2,6-Dideoxy-4-*O*-methylsulfonyl-α-D-*lyxo*-hexopyranoside (4). Methyl 3-*O*-benzoyl-2,6-dideoxy-α-D-*lyxo*-hexopyranoside[16] (0.28 g, 1.05 mmol), was treated with 0.25 mL of methanesulfonyl chloride in 1.0 mL of pyridine and 3 mL of ether. Isolation and purification as described in the general procedures for methanesulfonate preparation gave 0.26 g of methyl 3-*O*-benzoyl-2,6-dideoxy-4-*O*-methylsulfonyl-α-D-*lyxo*-hexopyranoside (**20**) (0.76 mmol, 72%): [α] = +130^0 (c = 0.51, EtOAc); R_f = 0.40 (ethyl acetate - hexane, 2:3); mp 132-133 ^{0}C; ^{1}H NMR δ 1.34 (H_6, $J_{5,6}$ = 6.5 Hz), 2.18 (H_{2a}, $J_{1,2a}$ = 3.5

Hz, $J_{2a,\ 2e}$ = 12.5 Hz, $J_{2a,3}$ = 12.5 Hz), 2.05 (H_{2e}, $J_{1,2e}$ = 1.1 Hz, $J_{2e,3}$ = 5.0 Hz), 3.03 (CH_3SO_3), 3.38 (OMe), 4.16 (H_5, $J_{5,6}$ = 6.5 Hz), 5.53 (H_3, $J_{3,4}$ = 2.7 Hz), 5.02 (H_4), 4.91 (H_1); ^{13}C NMR δ 17.22 (C_6), 29.84 (C_2), 38.86 (CH_3SO_3), 55.07 (OCH_3), 64.62 (C_5), 67.25 (C_3), 78.84 (C_4), 98.37 (C_1), 128.37-133.28 (aromatic), 165.72 (C=O). Anal. Calcd for $C_{15}H_{20}O_7S$: C, 52.31; H, 5.85. Found: C, 52.08; H, 6.00.

Compound **20** (0.67 mmol), potassium iodide (1.8 mmol), and sodium bicarbonate (3.8 mmol) in 200 mL of methanol were irradiated according to the standard photolysis procedure. Isolation and purification as described in the general procedures for methanesulfonate preparation gave 0.67 mmol (98%) of compound **4**: [α] = +145^0 (c = 0.89, EtOAc); R_f = 0.23 (ethyl acetate - hexane, 3:2); mp 121-122 ^{0}C; ^1H NMR δ 1.30 (H_6, $J_{5,6}$ = 6.5 Hz), 2.18 (H_{2a}, $J_{1,2a}$ = 3.5 Hz, $J_{2a,\ 2e}$ = 12.5 Hz, $J_{2a,3}$ = 12.5 Hz), 2.05 (H_{2e}, $J_{1,2e}$ = 1.1 Hz, $J_{2e,3}$ = 5.0 Hz), 3.19 (CH_3SO_3), 3.33 (OMe), 3.99 (H_5, $J_{5,6}$ = 6.5 Hz), 4.19 (H_3, $J_{3,4}$ = 2.7 Hz), 4.76 (H_4), 4.81 (H_1); ^{13}C NMR δ 17.11 (C_6), 32.83 (C_2), 38.74 (CH_3SO_3), 55.03 (OCH_3), 64.49 (C_5), 64.35 (C_3), 81.97 (C_4), 98.57 (C_1).

Anal. Calcd for $C_8H_{16}O_6S$: C, 39.99; H, 6.73. Found: C, 40.20; H 6.87.

Methyl 2,6-Dideoxy-3-*O*-(2-methoxyethoxymethyl)-4-*O*-methylsulfonyl-α-D-*arabino*-hexopyranoside (5). Methyl 2,6-dideoxy-4-*O*-methylsulfonyl-α-D-*arabino*-hexopyranoside[12] (0.35 g, 1.46 mmol), 0.65 g of 2-methoxyethoxymethyl chloride (MEM chloride) (5.2 mmol), and 0.88 g of *N,N*-diisopropylethylamine (6.8 mmol) in 10 mL of dichloromethane were reacted for 14 h. Isolation and purification as described in the general procedures for methanesulfonate preparation gave compound **5** (1.31 mmol, 90%): [α] = +113^0 (c = 0.68, EtOAc); R_f = 0.21 (ethyl acetate - hexane, 2:3); ^1H NMR δ 1.34 (H_6, $J_{5,6}$ = 6.3 Hz), 1.76 (H_{2a}, $J_{1,2a}$ = 3.7 Hz, $J_{2a,\ 2e}$ = 13.1 Hz, $J_{2a,3}$ = 11.4 Hz), 2.39 (H_{2e}, $J_{1,2e}$ = 1.1 Hz, $J_{2e,3}$ = 5.3 Hz), 3.09 (CH_3SO_3), 3.31 (OMe), 3.39 (OMe on MEM group), 3.52 - 3.60 (CH_2CH_2), 3.83 (H_5, $J_{5,6}$ = 6.3 Hz, $J_{4,5}$ = 9.5 Hz), 4.06 (H_3, $J_{3,4}$ = 9.4

Hz), 4.22 (H_4); 4.72 (H_1), 4.80 (OCH_2); ^{13}C NMR δ 17.85 (C_6), 36.80 (C_2), 38.84 (CH_3SO_3), 54.78 (OCH_3), 59.00 (OCH_3 on MEM group), 65.68 (C_5), 67.48, 71.72 (CH_2CH_2), 73.47 (C_3), 84.60 (C_4), 95.15 (OCH_2O on MEM group), 97.84 (C_1).

Anal. Calcd for $C_{12}H_{24}O_8S$: C, 43.89; H, 7.37. Found: C, 43.99; H 7.30.

1,2-*O*-Isopropylidene-3-*O*-methylsulfonyl-α-D-glucofuranose (6). 1,2:5,6-Di-*O*-isopropylidene-3-*O*-methylsulfonyl-α-D-glucofuranose[9] (6.0 g, 18 mmol) was dissolved in 100 mL of methanol and 100 mL of dilute sulfuric acid (0.8%). After stirring at room temperature for 30 h, the mixture was neutralized with sodium carbonate. After most of the solvent was removed under reduced pressure, the precipitate which formed was removed by filtration and washed with ethyl acetate (2 x 200 mL). The solvent was distilled from the combined filtrate and washings under reduced pressure to give **6** (4.1 g, 14 mmol, 78%). ^1H NMR δ (D_2O) 1.32, 1.51, (CMe_2), 3.18 (OH), 3.16 (CH_3SO_3), 3.48 (H_6), 3.73 ($H_{6'}$), 3.85 (H_5, $J_{4,5}$ = 9.5 Hz), 4.23 (H_4, $J_{3,4}$ = 2.7 Hz), 4.95 (H_2, $J_{1,2}$ = 3.7 Hz), 5.11 (H_3, $J_{2,3}$ = 2.8 Hz), 6.05 (H_1); ^{13}C NMR δ 26.18, 26.50 ($C(\underline{C}H_3)_2$), 38.10 (CH_3SO_3), 63.89 (C_6), 68.27 (C_4), 78.47 (C_5), 82.02 (C_3), 83.30 (C_2), 105.00 (C_1), 112.74 ($\underline{C}(CH_3)_2$).

Anal. Calcd for $C_{12}H_{24}O_8S$: C, 40.26; H, 6.08. Found: C, 40.59; H 6.30.

5,6-Di-*O*-acetyl-1,2-*O*-isopropylidene-3-*O*-methylsulfonyl-α-D-glucofuranose (13). Acetyl chloride (2.1 mL, 27 mmol) was added in a dropwise fashion to a cooled (ice water) solution of compound **6** (2.0 g, 6.7 mmol) in 4.5 mL of pyridine. After standing at room temperature for 1 h, the reaction mixture was added to a stirred solution of 50 mL of saturated sodium bicarbonate. The precipitate which formed was collected, dissolved in chloroform, and dried with magnesium sulfate. After removing the solvent under reduced pressure, the residue was chromatographed according to the standard procedure to give 2.2 g (5.8 mmol, 85%) of compound **13**, mp 117-120 °C, R_f = 0.31 (ethyl acetate - hexane, 2:3); ^1H NMR δ 1.33, 1.52, (CMe$_2$), 2.08 (COCH$_3$), 3.07 (CH$_3$SO$_3$), 4.11 (H$_6$, $J_{5,6}$ = 5.3 Hz, $J_{6,6'}$ = 12.4 Hz), 4.48 (H$_4$, $J_{3,4}$ = 2.9 Hz, $J_{4,5}$ = 9.5 Hz), 4.59 (H$_{6'}$, $J_{5,6'}$ = 2.4 Hz), 4.84 (H$_2$, $J_{1,2}$ = 3.6 Hz), 5.12 (H$_3$, $J_{3,4}$ = 2.9 Hz), 5.24 (H$_5$, $J_{4,5}$ = 9.5 Hz), 5.97 (H$_1$); ^{13}C NMR δ 20.70, 22.90 (CO$\underline{C}$H$_3$), 26.27, 26.66 (C($\underline{C}$H$_3$)$_2$), 38.26 (CH$_3$SO$_3$), 63.17 (C$_6$), 67.17 (C$_5$), 76.49 (C$_4$), 78.45 (C$_3$), 82.85 (C$_2$), 105.21 (C$_1$), 112.90 ($\underline{C}$(CH$_3$)$_2$), 170.05, 170.55 ($\underline{C}$OCH$_3$).

5,6-Di-*O*-benzoyl-1,2-*O*-isopropylidene-3-*O*-methylsulfonyl-α-D-glucofuranose (14). Benzoyl chloride (4.2 mL, 12 mmol) was added in a dropwise fashion to a cooled (ice water) solution of 1.1 g of compound **6** (4.0 mmol) in 4.5 mL of pyridine. After standing at room temperature for 44 h, the reaction mixture was added to a stirred solution of 75 mL of saturated sodium bicarbonate. The aqueous solution was decanted and the residue dissolved in 50 mL of ethyl acetate and dried over magnesium sulfate. After removing the solvent under reduced pressure, the residue was chromatographed according to the standard procedure to give 1.84 g (3.6 mmol, 87%) of compound **14**, R_f = 0.22 (ethyl acetate - hexane, 3:7), $[\alpha]$ = +2.2^0 (c = 0.60 ethyl acetate); ^{1}H NMR δ 1.34, 1.54, (CMe$_2$), 3.02 (CH$_3$SO$_3$), 4.53 (H$_6$, $J_{5,6}$ = 5.6 Hz, $J_{6,6'}$ = 12.4 Hz), 4.73 (H$_4$, $J_{3,4}$ = 2.9 Hz, $J_{4,5}$ = 9.4 Hz), 4.93 (H$_{6'}$, $J_{5,6'}$ = 2.3 Hz), 4.90 (H$_2$, $J_{1,2}$ = 3.1 Hz), 5.15 (H$_3$, $J_{3,4}$ = 2.9 Hz), 5.68 (H$_5$, $J_{4,5}$ = 9.4 Hz), 5.97 (H$_1$), 7.38 - 8.01 (aromatic); ^{13}C NMR δ 26.26, 26.65 (C($\underline{C}$H$_3$)$_2$), 38.31 (CH$_3$SO$_3$), 63.87 (C$_6$), 68.06 (C$_5$), 76.82 (C$_4$), 79.39 (C$_3$), 82.97 (C$_2$), 105.16 (C$_1$), 112.96 ($\underline{C}$(CH$_3$)$_2$), 128.4 - 133.52 (aromatic).

5,6-Di-*O*-benzyl-1,2-*O*-isopropylidene-3-*O*-methylsulfonyl-α-D-glucofuranose (16). Benzyl bromide (1.1 mL, 10 mmol), sodium hydride (0.5 g, 20 mmol), and compound **6** (1.0 g, 3.4 mmol) were combined in 25 mL of *N,N*-dimethylformamide and the mixture was stirred at room temperature for 3 h. Water (25 mL and methanol (25 mL) were added and the reaction mixture was extracted with 3 x 50 mL of ethyl ether. The combined extracts were dried over magnesium sulfate, the solvent removed under reduced pressure, and the residue chromatographed in the standard fashion to give **16** (2.9 mmol, 84%) R_f = 0.40 (ethyl acetate - hexane, 2:3), [α] = -21.0^0 (c = 0.19 ethyl acetate); ^{1}H NMR δ 1.30, 1.48, (CMe_2), 2.83 (CH_3SO_3), 3.67 (H_6, $J_{5,6}$ = 4.8 Hz, $J_{6,6'}$ = 10.9 Hz), 4.46 (H_4, $J_{3,4}$ = 2.8 Hz, $J_{4,5}$ = 9.3 Hz, $J_{4,5}$ = 9.3 Hz), 3.90 ($H_{6'}$, $J_{5,6'}$ = 1.8 Hz), 4.57 ($ArCH_2$) 4.83 (H_2, $J_{1,2}$ = 3.5 Hz), 5.10 (H_3, $J_{2,3}$ = 2.8 Hz), 5.93 (H_1), 7.19 -7.40 (aromatic); ^{13}C NMR δ 26.28, 26.51 ($C(\underline{C}H_3)_2$), 38.00 (CH_3SO_3), 69.56 (C_6), 71.64, 73.38 ($Ar\underline{C}H_2$), 74.95 (C_5), 77.32 (C_4), 81.78 (C_3), 82.99 (C_2), 104.62 (C_1), 112.53 ($\underline{C}(CH_3)_2$), 127.6 - 138.12 (aromatic).

Anal. Calcd for $C_{24}H_{30}O_8S$: C, 60.23; H, 6.32. Found: C, 60.55; H 6.50.

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