were determined with the following spectrometers: UCB-200 and UCB-250 (super-conducting, FT instruments operating at 200 and 250 MHz). Chemical shifts are expressed in ppm downfield from tetramethylsilane using tetramethylsilane as an internal standard for ^{1}H NMR and chloroform (77.0) for ^{13}C NMR. ^{1}H NMR data are tabulated in the order of: multiplicity (s, singlet; d, doublet; t, triplet, q, quartet; m, multiplet), number of protons, coupling constants in hertz. The ultrasonic waves were produced by a 250-W high-intensity ultrasonic processor, Vibra Cell from Sonics & Materials Inc. During our reactions the power meter showed an average power of 23% corresponding to a power of about 45 W cm^{-2}. Ultrasonic irradiation was carried out with the tip of the horn immersed directly in the solution.

General Procedure for the Decomposition of Esters by Sonication. The ester was dissolved in the solvent system listed and irradiated with ultrasonic waves under an argon atmosphere until thin-layer chromatography indicated complete consumption of starting ester.[10] A 20 °C water bath was kept around the reaction vessel during sonication, and this maintained the internal reaction temperature at 20 °C up to a maximum of 35 °C. Aluminum foil was used to surround the reaction vessel to completely exclude light from the reaction mixture. There was no need to stir the reaction mixture during the sonication process. The solvent was then evaporated under reduced pressure, and the residue was purified by chromatography on silica gel using a solvent gradient, generally pentane, followed by ethyl acetate–pentane mixtures. The compounds obtained by this method are listed below.

Pentadecane (2). Sonication of a solution of ester 1 (0.105 g, 0.287 mmol), carbon tetrachloride (10 mL), and thiophenol (0.088 mL, 0.857 mmol, 3 equiv) for 20 min gave, after chromatography (pentane), fractions A and B.

Fraction A contained **2** as a clear liquid (0.051 g, 85%): identical with an authentic sample.

Fraction B contained **5** as yellow-white crystals (0.088 g, 70%): identical with an authentic sample.

The column was further eluted (ethyl acetate) to give **4** as a yellowish solid (0.028 g, 87%): identical with an authentic sample.

Pentadecylselenobenzene (6) and 1-Chloropentadecane (7). Sonication of a solution of ester 1 (0.26 mmol, 1.0 equiv), carbon tetrachloride (10 mL), and diphenyl diselenide (0.26 mmol, 1.0 equiv or 0.52 mmol, 2.0 equiv) for 30 min gave, after chromatography (pentane), **6** (77% or 80%, see table) [^{1}H NMR (200 MHz, $CDCl_3$) δ 0.90 (t, 3, J = 7.0 Hz), 1.2–1.4 (m, 24), 1.72 (tt, 2, J = 7.0, 7.0 Hz), 2.95 (t, 2, J = 7.0 Hz), 7.26 (m, 3), 7.53 (m, 2); identical with the published spectrum[8a]] and **7** (10% or 0%, see table), identical with an authentic sample.[4]

The column was further eluted (pentane 90%, ethyl acetate 10%) to give **8** (68–88%, see table): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.02–7.08 (m, 1), 7.26–7.29 (m, 3), 7.57–7.69 (m, 4), 8.45–8.47 (m, 1); ^{13}C NMR (200 MHz, $CDCl_3$) δ 149.40, 137.11, 131.61, 129.82, 129.24, 127.73, 121.27, 120.62; decomposed slowly during chromatography.

The column was further eluted (pentane 90%, ethyl acetate 10%) to give **9** (8–14%, see table): identical with an authentic sample.[4]

Pentadecylthiobenzene (10) and 1-Chloropentadecane (7). Sonication of a solution of ester 1 (0.107 g, 0.29 mmol, 1.0 equiv), carbon tetrachloride (10 mL), and diphenyl disulfide (0.58 mmol, 2.0 equiv or 1.45 mmol, 5.0 equiv) for 30 min gave, after chromatography (pentane), **7** (91% or 80%, see table) mixed with a small amount of **10** (2% or 8%, see table): mp 49–50 °C (lit.[8a] mp 51 °C).

The column was further eluted (pentane 90%, ethyl acetate 10%) to give **3** (3% or 8%, see table): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.06–7.13 (m, 1), 7.22–7.35 (m, 3), 7.49–7.68 (m, 4), 8.46–8.48 (m, 1); ^{13}C NMR (200 MHz, $CDCl_3$) δ 149.56, 149.45, 137.26, 137.21, 129.09, 127.23, 120.84, 119.48. Anal. Calcd C, 60.24; H, 4.14; N, 6.39. Found: C, 60.26; H, 4.24, N, 6.21.

The column was further eluted (pentane 90%, ethyl acetate 10%) to give **9** (70% or 73%, see table).

Reduction of 3 with Thiophenol. In 2 mL of CCl_4 was dissolved **3** (32 mg, 0.15 mmol) followed by thiophenol (16 mg, 0.15 mmol). The solution turned yellow, and ^{1}H NMR (200 MHz, $CDCl_3$) of the concentrated solution indicated the presence of only **4** and **5**.

(10) No reactions occurs if the reaction solution was allowed to stand without irradiation at room temperature.

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A Light-Initiated Process for Rapid Debenzylation of Carbohydrates

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During the synthesis of several disaccharides to be used in the preparation of analogues of the anticancer agent mithramycin (1), difficulties (slow and sometimes incomplete reaction) were encountered with catalytic hydrogenolysis, the traditional method for removal of benzyl protecting groups. Although these difficulties, which have been known for some time to accompany occasionally the hydrogenolysis of benzyl ethers,[1,2] were not insurmountable, they created sufficient inconvenience to stimulate interest in other debenzylation reactions. A number of alternatives to catalytic hydrogenolysis have been reported. These include reaction with molecular bromine,[3] sodium in liquid ammonia,[1] boron trifluoride etherate,[4] iodotrimethylsilane (followed by hydrolysis),[5] ferric chloride,[6] ruthenium tetraoxide,[7] and ozone.[8] Other known methods involve electrochemical oxidation,[9] catalytic transfer hydrogenation,[2,10,11] and homogeneous electron transfer.[12]

The ease with which β-linked disaccharides constructed from 2,6-dideoxy sugars undergo acid-catalyzed reaction discouraged use of some of the reported debenzylation reactions while other methods were eliminated from consideration by the facility with which acyl groups are removed under basic conditions. Even with these restrictions, several of the known debenzylation methods remained viable possibilities; in addition, another reaction, developed several years ago for the conversion of benzylidene acetals into benzoate esters,[13] also seemed promising. In this reaction the acetals were partially deprotected by photolysis in the presence of *N*-bromosuccinimide, barium carbonate, and water (eq 1). These same conditions appeared to satisfy the requirements placed on the desired debenzylation reaction and seemed likely to provide an effective method for removal of benzyl groups.

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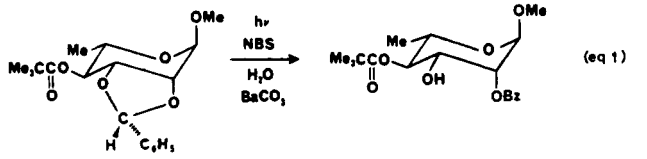
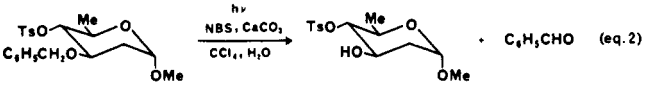
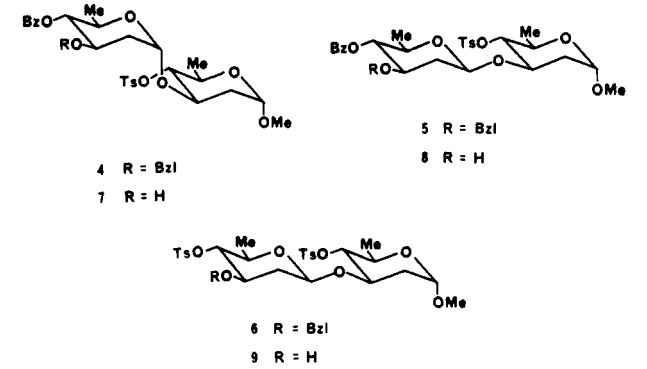


When a rapidly stirred suspension of calcium carbonate in a carbon tetrachloride solution of *N*-bromosuccinimide and methyl 3-*O*-benzyl-2,6-dideoxy-3-*O*-(*p*-tolylsulfonyl)-α-D-*arabino*-hexopyranoside (**2**) was irradiated with a 375-W incandescent lamp for 15 min, complete loss of the benzyl group occurred to give methyl 2,6-dideoxy-3-*O*-(*p*-tolylsulfonyl)-α-D-*arabino*-hexopyranoside (**3**) in 86% yield (eq 2). Reaction of the disaccharides **4**, **5**, and

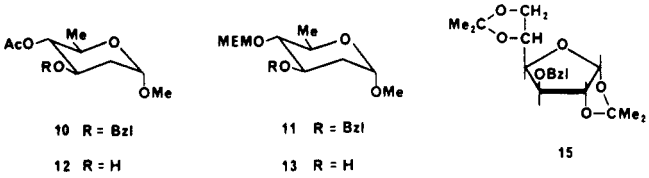


2 3

6 under the same conditions produced the corresponding deprotected compounds **7**, **8**, and **9** in 100%, 91%, and 95% yields, respectively.



The success of this debenzylation procedure with compounds **2** and **4**–**6** raised the possibility of its usefulness when other protecting groups were involved; thus, several additional compounds containing common protecting groups were studied. Debenzylation of methyl 4-*O*-acetyl-3-*O*-benzyl-2,6-dideoxy-α-D-*arabino*-hexopyranoside (**10**) and methyl 3-*O*-benzyl-2,6-dideoxy-4-*O*-(2-methoxyethoxy)methyl)-α-D-*arabino*-hexopyranoside (**11**) gave the corresponding deprotected compounds **12** and **13** in 85% and 86% yields, respectively. 3-*O*-Benzyl-1,2:5,6-di-*O*-



isopropylidene-α-D-glucofuranose (**14**) was debenzylated in 60% yield. This photochemically initiated debenzylation is similar to (but avoids the strongly acidic conditions) the deprotection process reported by BeMiller and coworkers,[3] who used molecular bromine rather than NBS, and it is also related to the formation of glycosyl bromides from benzyl glycosides reported by Hashimoto and coworkers.[14]

Experimental Section

General Procedures. Unless otherwise noted, ^{1}H NMR and ^{13}C NMR spectra were determined using a Varian FT-80A spectrometer with $CDCl_3$ as the solvent. Chemical shifts are relative to tetramethylsilane (δ = 0.0). Mass spectral data were collected on a Finnigan TSQ-45 triple quadrupole mass spectrometer. Column chromatography was conducted using a 2.5 × 15 cm column of Baker 240–400 mesh silica gel with hexane–ethyl acetate (3:1) as the developer. TLC was done using Whatman silica gel 60 A plates developed with hexane–ethyl acetate (1:1). Optical rotations were determined for solutions in chloroform at 22 °C using a Perkin-Elmer Model 241 spectrometer.

Synthesis of Methyl 3-*O*-(3-*O*-Benzyl-2,6-dideoxy-4-*O*-(*p*-tolylsulfonyl)-β-D-*arabino*-hexopyranosyl)-2,6-dideoxy-4-*O*-(*p*-tolylsulfonyl)-α-D-*arabino*-hexopyranoside (6). Methyl 3-*O*-(3-*O*-benzyl-2,6-dideoxy-β-D-*arabino*-hexopyranosyl)-2,6-dideoxy-4-*O*-(*p*-tolylsulfonyl)-α-D-*arabino*-hexopyranoside[15] (0.80 g, 1.49 mmol) and 1.00 g of *p*-toluenesulfonyl chloride were dissolved in 25 mL of pyridine and heated at 70 °C for 14 h. After cooling and addition of 1.0 mL of water, the reaction mixture was added slowly to a rapidly stirred solution of 1.0 g of sodium bicarbonate in 200 mL of water. The precipitate that formed was collected and recrystallized from ethanol to give 0.98 g (1.42 mmol, 95% yield) of compound **6**: mp 148–150 °C; R_f = 0.61; $[\alpha]_D$ +56° (*c* 0.86); ^{1}H NMR (300 MHz) δ 0.73 ($H_{2a'}$, $J_{1',2a'}$ = 9.9 Hz, $J_{2a',3'}$ = 11.6 Hz), 1.22 ($H_{6'}$, $J_{5',6'}$ = 6.2 Hz), 1.41 (H_6, $J_{5,6}$ = 6.3 Hz), 1.54 (H_{2a}, $J_{1,2a}$ = 3.6 Hz, $J_{2a,3}$ = 11.4 Hz), 1.82 ($H_{2e'}$, $J_{1',2e'}$ = 2.0 Hz, $J_{2e',3'}$ = 5.3 Hz), 2.10 (H_{2e}, $J_{1,2e}$ = 1.0 Hz, $J_{2e,3}$ = 5.2 Hz), 2.33 and 2.52 (ArCH_3), 3.16 ($H_{5'}$, $J_{4',5'}$ = 9.5 Hz), 3.25 ($H_{3'}$, $J_{3',4'}$ = 9.1 Hz), 3.29 (OCH_3), 3.82 (H_5, $J_{4,5}$ = 9.5 Hz), 4.04 and 4.21 (ArCH_2), 4.05 ($H_{4'}$), 4.07 (H_3, $J_{3,4}$ = 9.3 Hz), 4.17 ($H_{1'}$), 4.27 (H_4), 4.70 (H_1), 7.00–7.36 and 7.74–7.82 (aromatic); ^{13}C NMR δ 17.81, 17.94 (C_6, $C_{6'}$), 21.57, 21.57 (ArCH_3), 35.22 (C_2), 36.24 ($C_{2'}$), 54.68 (OCH_3), 65.99 (C_5), 69.68, 70.08 (C_3, $C_{5'}$), 70.65 (CH_2), 75.21 ($C_{3'}$), 83.83, 84.19 (C_4, $C_{4'}$), 94.75 ($C_{1'}$), 97.65 (C_1), 127.31, 127.54, 127.76, 128.20, 128.46, 129.35, 134.96, 135.21, 137.81, 144.30, 144.44 (aromatic carbons). Anal. Calcd for $C_{34}H_{42}O_{11}S_2$: C, 59.11; H, 6.13. Found: C, 59.27; H, 6.00.

Debenzylation of Methyl 3-*O*-Benzyl-2,6-dideoxy-4-*O*-(*p*-tolylsulfonyl)-α-D-*arabino*-hexopyranoside (2).[15] Compound **2** (3.00 g, 7.38 mmol) and 1.84 g (10.3 mmol) of *N*-bromosuccinimide were dissolved in 100 mL of carbon tetrachloride in which 5 mL of water and 3.25 g (32.5 mmol) of calcium carbonate were suspended by rapid stirring. The solution was purged with nitrogen for 1 h and then irradiated for 15 min with a 375-W incandescent lamp. After removal of the solids by filtration and distillation of the solvent, the residue was chromatographed to give 2.00 g (6.35 mmol, 86%) of methyl 2,6-dideoxy-4-*O*-(*p*-tolylsulfonyl)-α-D-*arabino*-hexopyranoside (**3**), mp 126 °C (lit.[16] mp 126 °C), identical in ^{1}H NMR spectrum[17] and ^{13}C NMR spectrum[15] with an independently synthesized sample.[15]

Debenzylation of Methyl 3-*O*-(4-*O*-Benzoyl-3-*O*-benzyl-2,6-dideoxy-α-D-*arabino*-hexopyranosyl)-2,6-dideoxy-4-*O*-(*p*-tolylsulfonyl)-α-D-*arabino*-hexopyranoside (4). Compound **4**[15] (0.59 g, 0.92 mmol) and 0.27 g (1.51 mmol) of *N*-bromosuccinimide were dissolved in 300 mL of carbon tetrachloride, in which 5 mL of water and 0.35 g (3.50 mmol) of calcium carbonate were suspended, and were irradiated and purified as described for compound **2** to give 0.51 g (0.92 mmol, 100%) of methyl 3-*O*-(4-*O*-benzoyl-2,6-dideoxy-α-D-*arabino*-hexopyranosyl)-2,6-dideoxy-4-*O*-(*p*-tolylsulfonyl)-α-D-*arabino*-hexopyranoside (**7**): ^{13}C NMR δ 17.59, 18.07 (C_6, $C_{6'}$), 21.57 (ArCH_3), 37.66, 37.84 (C_2, $C_{2'}$), 54.68 (OCH_3), 65.67, 66.19 (C_5, $C_{5'}$), 67.31 (C_3), 74.61 ($C_{3'}$), 79.38 ($C_{4'}$), 84.67 (C_4), 97.83 ($C_{1'}$), 99.55 (C_1), 127.51, 128.48, 129.87, 133.31, 135.31, 144.87 (aromatic), 166.84 (C=O); ^{1}H NMR δ 1.17, 1.18 (H_6, $H_{6'}$), 2.41 (ArCH_3), 3.27 (OCH_3), 4.38 ($H_{4'}$, $J_{3',4'}$ = $J_{4',5'}$ = 9.2 Hz), 4.68 ($H_{1'}$, $J_{1',2a'}$ = 2.8 Hz), 4.72 (H_4, $J_{3,4}$ = $J_{4,5}$ = 9.4 Hz), 4.88 (H_1, $J_{1,2a}$ = 2.7 Hz), 7.18–8.11 (aromatic). Anal. Calcd for $C_{27}H_{34}O_{10}S_2$: C, 58.89; H, 6.22. Found: C, 58.80; H, 6.02.

Debenzylation of Methyl 3-*O*-(4-*O*-Benzoyl-3-*O*-benzyl-2,6-dideoxy-β-D-*arabino*-hexopyranosyl)-2,6-dideoxy-4-*O*-(*p*-tolylsulfonyl)-α-D-*arabino*-hexopyranoside (5). Compound **5**[15] (0.16 g, 0.25 mmol) was debenzylated according to the irra-

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diation and isolation procedure described for compound 4 to give 0.13 g (0.23 mmol, 91%) of methyl 3-*O*-(4-*O*-benzoyl-2,6-dideoxy-β-D-*arabino*-hexopyranosyl)-2,6-dideoxy-4-*O*-(*p*-tolylsulfonyl)-α-D-*arabino*-hexopyranoside (8), identical in NMR spectra (^{1}H and ^{13}C) and purity with an authentic sample of 8 obtained by hydrogenolysis.[15]

Debenzylation of Methyl 2,6-Dideoxy-3-*O*-(2,6-dideoxy-4-*O*-(*p*-tolylsulfonyl)-β-D-*arabino*-hexopyranosyl)-4-*O*-(*p*-tolylsulfonyl)-α-D-*arabino*-hexopyranoside (6). Compound 6 (0.80 g, 1.16 mmol) and 0.27 g (1.51 mmol) of *N*-bromosuccinimide were reacted, and the product was purified as described for compound 4 to give 0.59 g (1.10 mmol, 95%) of methyl 2,6-dideoxy-3-*O*-(2,6-dideoxy-4-*O*-(*p*-tolylsulfonyl)-β-D-*arabino*-hexopyranosyl)-4-*O*-(*p*-tolylsulfonyl)-α-D-*arabino*-hexopyranoside (9): mp 106–108 °C; R_f 0.13; ^{13}C NMR (acetone-d_6) δ 18.27, 18.59 (C_6, $C_{6'}$), 21.67, 21.86 ($ArCH_3$), 35.90 (C_2), 40.32 ($C_{2'}$), 55.03 (OCH_3), 66.79 (C_5), 69.07, 70.11, 71.24 (C_3, $C_{3'}$, C_5), 85.37 (C_4), 87.50 ($C_{4'}$), 95.86 ($C_{1'}$), 98.86 (C_1), 129.31, 129.75, 130.75, 130.96, 136.35, 136.82, 145.91 (aromatic carbons); ^{1}H NMR (acetone-d_6) δ 0.81 ($H_{2a'}$, $J_{1',2a'}$ = 11.6 Hz, $J_{2a',3'}$ = 9.9 Hz), 1.09 (H_6, $J_{5,6}$ = 6.2 Hz), 1.36 ($H_{6'}$, $J_{5',6'}$ = 6.2 Hz), 1.51 (H_{2a}, $J_{1,2a}$ = 3.6 Hz, $J_{2a,3}$ = 10.8 Hz), 1.75 ($H_{2e'}$, $J_{1',2e'}$ = 1.9 Hz, $J_{2e',3'}$ = 5.4 Hz), 2.20 (H_{2e}, $J_{1,2e}$ = 1.0 Hz, $J_{2e,3}$ = 5.2 Hz), 2.45, 2.57 ($ArCH_3$), 3.28 (OCH_3), 4.20 (H_4, $J_{4,5}$ = $J_{3,4}$ = 9.0 Hz), 4.46 ($H_{1'}$), 4.71 (H_1), 4.9 ($H_{4'}$, $J_{3',4'}$ = $J_{4',5'}$ = 9.2 Hz), 7.39–7.49 and 7.78–7.89 (aromatic). Anal. Calcd for $C_{27}H_{36}O_{11}S_2$: C, 53.98; H, 6.04. Found: C, 53.55; H, 6.11.

Methyl 4-*O*-Acetyl-3-*O*-benzyl-2,6-dideoxy-α-D-*arabino*-hexopyranoside (10). Methyl 3-*O*-benzyl-2,6-dideoxy-α-D-*arabino*-hexopyranoside (0.82 g, 3.25 mmol), prepared according to the procedure of Monneret et al.,[18] was dissolved in 10 mL of pyridine, and 1.0 g (13 mmol) of acetyl chloride was added in a dropwise manner to the rapidly stirred solution. The reaction mixture was allowed to stand for 14 h at room temperature, and then 1 mL of water was added to the stirred solution, which was cooled in an ice bath. The entire reaction mixture then was poured slowly into 200 mL of a rapidly stirred solution of saturated sodium bicarbonate. The solution was extracted three times with chloroform (50 mL), the solvent was distilled from the combined organic extracts, and the residue was chromatographed in the standard fashion to give 0.86 g (2.93 mmol, 90%) of compound 10: R_f 0.56; ^{13}C NMR δ 17.63 (C_6), 20.99 (CH_3CO), 35.53 (C_2), 54.64 (CH_3O), 65.84 (C_5), 71.30 (CH_2), 74.28 (C_3), 76.33 (C_4), 98.31 (C_1), 127.36, 127.49, 128.33 (aromatic), 170.09 (C=O); ^{1}H NMR δ 1.16 (H_6, $J_{5,6}$ = 6.3 Hz), 1.71 (H_{2a}, $J_{1,2a}$ = 3.6 Hz, $J_{2a,2e}$ = 13.2 Hz, $J_{2a,3}$ = 11.2 Hz), 2.01 (CH_3CO), 2.27 (H_{2e}, $J_{1,2e}$ = 1.4 Hz, $J_{2e,3}$ = 5.2 Hz), 3.29 (OCH_3), 3.46–3.99 (H_3, H_5), 4.50, 4.55 (CH_2), 4.74 (H_1), 4.76 (H_4, $J_{3,4}$ = $J_{4,5}$ = 9.4 Hz); exact mass calcd for $C_{16}H_{22}O_5$ 294.1468, found 294.1547.

Methyl 3-*O*-Benzyl-2,6-dideoxy-4-*O*-((2-methoxyethoxy)methyl)-α-D-*arabino*-hexopyranoside (11). Methyl 3-*O*-benzyl-2,6-dideoxy-α-D-*arabino*-hexopyranoside[18] (0.84 g, 3.3 mmol) and *N*,*N*-diisopropylethylamine (1.93 g, 15 mmol) were dissolved in 20 mL of dichloromethane, and 1.24 g (10 mmol) of (2-methoxyethoxy)methyl chloride was added to the stirred solution. The reaction mixture was heated under reflux for 14 h. The solvent was distilled under reduced pressure, and the residue was chromatographed in the normal fashion to give 0.91 g (2.7 mmol, 81%) of compound 11: R_f 0.39; ^{13}C NMR δ 17.89 (C_6), 34.87 (C_2), 54.52 (OCH_3, anomeric), 58.99 (OCH_3), 66.89 (C_5), 67.78, (C_3), 71.32 ($ArCH_2$), 71.78, 77.14 (OCH_2CH_2O), 81.49 (C_4), 97.06 (OCH_2O), 98.26 (C_1), 127.04, 127.84, 138.20 (aromatic); ^{1}H NMR δ 1.27 (H_6, $J_{5,6}$ = 6.1 Hz), 1.59 (H_{2a}, $J_{1,2a}$ = 3.6 Hz, $J_{2a,3}$ = 11.2 Hz, $J_{2a,2e}$ = 13.0 Hz), 2.33 (H_{2e}, $J_{1,2e}$ = 1.4 Hz, $J_{2e,3}$ = 5.0 Hz), 3.27, 3.32 (OCH_3), 4.54, 4.51 (OCH_2O), 4.70 (H_1), 7.27 (aromatic); exact mass calcd for $C_{18}H_{29}O_6$ (MH^+) 341.1964, found 341.2015.

Debenzylation of Compound 10. Compound 10 (0.53 g, 1.8 mmol) and 0.45 g (2.52 mmol) of *N*-bromosuccinimide were irradiated, and the reaction mixture was chromatographed as described for compound 2 to give 0.31 g (1.5 mmol, 85%) of methyl 4-*O*-acetyl-2,6-dideoxy-α-D-*arabino*-hexopyranoside (12): R_f 0.10; ^{13}C NMR δ 17.63 (C_6), 21.05 (CH_3CO), 38.28 (C_2), 54.74 (OCH_3), 65.42 (C_5), 67.48 (C_3), 78.99 (C_4), 98.29 (C_1); ^{1}H NMR δ 1.18 (H_6, $J_{5,6}$ = 6.2 Hz), 1.71 (H_{2a}, $J_{1,2a}$ = 3.6 Hz, $J_{2a,3}$ = 11.3 Hz, $J_{2a,2e}$ = 13.1), 2.12 (CH_3CO), 3.32 (OCH_3), 4.52 (H_4, $J_{3,4}$ = $J_{4,5}$ = 9.3 Hz), 4.75 (H_1); exact mass calcd for $C_9H_{16}O_5$ 204.0997, found 204.0949.

Debenzylation of Compound 11. Compound 11 (0.37 g, 1.09 mmol) and 0.25 g (1.4 mmol) of *N*-bromosuccinimide were irradiated, and the reaction mixture was chromatographed as described for compound 2 to give 0.23 g (0.94 mmol, 86%) of methyl 2,6-dideoxy-4-*O*-((2-methoxyethoxy)methyl)-α-D-*arabino*-hexopyranoside (13): R_f 0.07; ^{13}C NMR δ 17.87 (C_6), 37.05 (C_2), 54.59 (OCH_3, anomeric), 58.97 OCH_3), 65.89 (C_5), 67.87 (C_3), 67.23, 71.57 (OCH_2CH_2O), 89.04 (C_4), 97.26 (OCH_2O), 98.36 (C_1); ^{1}H NMR δ 1.25 (H_6, $J_{5,6}$ = 6.2 Hz), 1.63 (H_{2a}, $J_{1,2a}$ = 3.6 Hz, $J_{2a,3}$ = 11.5 Hz, $J_{2a,2e}$ = 13.2 Hz), 2.18 (H_{2e}, $J_{1,2e}$ = 1.2 Hz, $J_{2e,3}$ = 5.5 Hz), 2.91 (H_4, $J_{3,4}$ = $J_{4,5}$ = 9.0 Hz), 3.31 (OMe), 3.38 (OMe), 4.74 (H_1), 4.74, 4.92 (OCH_2O); exact mass calcd for $C_{11}H_{23}O_6$ (MH^+) 251.1493, found 251.1440.

Debenzylation of 3-*O*-Benzyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (14).[19] Compound 14 (0.52 g, 1.48 mmol) and 0.53 g (3.0 mmol) of *N*-bromosuccinimide were dissolved in 100 mL of carbon tetrachloride, and the reaction mixture was stirred for 1 h while being purged with nitrogen. The nitrogen purge was continued during 1 h of irradiation. After irradiation, the reaction mixture was poured into 20 mL of rapidly stirred, saturated sodium bicarbonate solution. The layers were separated, and the aqueous layer was extracted with 30 mL of chloroform. The solvent was distilled from the combined organic extracts, and the residue was chromatographed by the standard procedure to give 0.23 mg (0.90 mmol, 60%) of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose, mp 106–108 °C (lit.[5] mp 106–108 °C). The ^{1}H NMR spectrum of this material also was identical with that of the authentic sample.[20]

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Registry No. 2, 121330-33-4; 3, 14624-27-2; 4, 121330-38-9; 5, 121330-37-8; 6, 123567-40-8; 6 (monotosyl deriv), 121330-39-0; 7, 123567-41-9; 8, 121330-41-4; 9, 123567-42-0; 10, 123567-43-1; 10 (deacetyl deriv), 90762-83-7; 11, 123567-44-2; 12, 123567-45-3; 13, 123567-46-4; 14, 18685-18-2; 14 (debenzylated deriv), 582-52-5; (2-methoxyethoxy)methyl chloride, 3970-21-6.

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Syntheses of Trifluoromethylated Pyridinones and Pyrimidinones

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Although a large number of 6-(trifluoromethyl)uracils[1-5] and 6-(trifluoromethyl)-4(3*H*)-pyrimidinones[6,7] are known, there are few reported 2-(trifluoromethyl)-4(1*H*)-pyridinones[8-10] prior to our own investigation of the cy-

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