C-Allylation of 1- and 6-Bromosugars with Allylic Sulfides and Sulfones

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Reaction of the bromosugars 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide (**1**), methyl 2,3-anhydro-6-bromo-6-deoxy-α-D-allopyranoside (**2**), and methyl 2,3-anhydro-4-*O*-benzoyl-6-bromo-6-deoxy-α-D-allopyranoside (**3**) with the allylic sulfides and sulfones **4**−**9** in the presence of hexabutyldistannane under photolytic conditions gave the corresponding α-*C*-allyl galactosides **10**−**12** and the 6-C-allylated epoxysugars **13**, **15**, and **16** in 61−90% yield.

Introduction

Chain elongation of saccharides, via the formation of carbon−carbon bonds at positions 1 and 6, leads to chiral compounds of potential value for the synthesis of natural products and other important substances. Elongation at the 1-position gives *C*-glycosides (hydrolytically stable analogs of normal *O*-glycosides), a class of compounds that has been the subject of intense synthetic and biochemical interest recently, as witnessed by recent reviews.[1]

The intermolecular free radical-induced coupling of 1-bromopyranoses with acrylonitrile and similar compounds to give *C*-glycosides has been thoroughly investigated, largely through the work of Giese.[2,3] These reactions almost always lead to the exclusive formation of *C*-α-glycopyranosides.

Free radical allylation of 6-bromosugars was performed by Keck, using various allylstannanes and AIBN.[4] In an attempt to avoid the need for allylstannanes, a method was developed where allylic sulfides and alkyl halides were reacted in the presence of hexabutyldistannane (irradiation of the latter initiated the radical chain reaction).[5] Similar allylations were reported by Curran.[6] Despite the obvious potential for allylations using allyl sulfides, no such reactions seem to have been reported with halosugar substrates.

We now report the successful free radical allylation at both the 1- and 6-position of bromosugar substrates, using essentially Keck's procedure[5] with different allylic sulfides and sulfones. The epoxy alcohol products **13**−**15** are currently under investigation as substrates in ring-contractions leading to five-membered-ring α,β-unsaturated aldehydes.[7]

Results and Discussion

Allylation of 1−3. Photolysis of a mixture of acetobromogalactose **1**, the sulfides and sulfones **4**−**9**, and hexabutyldistannane at room temperature using a Pyrex filter gave in good yields the C-α-glycosides **10**−**12** (Table 1); none of the corresponding C-β-glycosides were isolated. Using the same reaction conditions with the 6-bromoepoxy alcohol **2**[8] gave the 6-alkylated galactosides **13**−**15**. The yields were high for **13** and **15**, whereas **14** could only be obtained in approximately 30% yield; unidentified byproducts accounted for the remaining material. When HO-4 was protected with a benzoyl group (**3**), the reaction gave the 6-alkylated compound **16** in good yield. Debenzoylation of **16** with ethanolic sodium ethoxide gave **14** (84%).

Starting Materials 1−9. Acetobromogalactose **1** is a well-known building block in carbohydrate chemistry. The 6-bromoepoxides **2** and **3** might seem more elusive but are in fact easily prepared.[8] We reported recently the synthesis, in 68% yield over five steps, of epoxyalcohol **2** on a large scale, starting from methyl α-D-glucopyranoside.[9]

The allyl sulfide **4** and sulfone **5** are commercially available. The acrylic ester sulfide[10] **6** and sulfone[11] **7** were prepared as described in the literature. 3-Bromo-2-(bromomethyl)propyl acetate[12] (**17**) was treated with tetrabutylammonium fluoride in acetonitrile to give, after distillation, 2-(bromomethyl)propen-1-yl acetate[13] (**18**) in 76% yield. In addition to being a strong base in aprotic solvents, F^- is nucleophilic enough to displace the bromine in **18** to a substantial degree, when the reaction mixture was left for more than 20 min. Therefore, aqueous calcium nitrate was added in order to quench F^- as soon as the elimination was completed (CaF_2 has a low solubility). Treatment of **18** with thiophenol in the presence of cesium carbonate,[14] essentially as in the preparation of the corresponding benzylthio analog,[13] gave the allylic sulfide acetate **8** in 98% yield. The sulfone acetate[13] **9** was prepared in 73% yield by treatment of **18** with sodium benzenesulfinate (Scheme 1).

Experimental Section

^{1}H-NMR-spectra were recorded at 23°C and 300 MHz using $CDCl_3$ as solvent and $CHCl_3$ as internal standard (δ 7.26), or

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(1) (a) Hanessian, S.; Pernet, A. G. *Adv. Chem. Biochem.* **1976**, *33*, 111. (b) Postema, M. H. R. *Tetrahedron* **1992**, *48*, 8545. (c) Levy, D. E.; Tang, C. *The Chemistry of C-Glycosides*; Baldwin, J. E.; Magnus, P. D., Eds.; Elsevier Science Ltd.: Oxford, 1995.

(2) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon−Carbon Bonds;* Baldwin, J. E., Ed.; Pergamon Press: New York, **1985**.

(3) Giese, B.; Linker, T.; Muhn, R. *Tetrahedron* **1989**, *45*, 935.

(4) (a) Keck, G. E.; Yates, J. B. *J. Am. Chem. Soc.* **1982**, *104*, 5829. (b) Keck, G. E.; Enholm, E. J.; Yates, J. B.; Wiley, M. R. *Tetrahedron* **1985**, *41*, 4079.

(5) Keck, G. E.; Byers, J. H. *J. Org. Chem.* **1985**, *50*, 5442.

(6) Curran, D. P.; Yoo, B. *Tetrahedron Lett.* **1992**, *33*, 6931.

(7) (a) Sundin, A.; Frejd, T.; Magnusson, G. *J. Org. Chem.* **1986**, *51*, 3927. (b) Magnusson, G. *Org. Prep. Proc. Int.* **1990**, *22*, 547.

(8) Hanessian, S. *Org. Synth.* **1987**, *65*, 243.

(9) Pontén, F.; Magnusson, G. *Acta Chem. Scand.* **1994**, *48*, 566.

(10) Feldman, K. S.; Bobo, J. S.; Tewalt, G. L. *J. Org. Chem.* **1992**, *57*, 4573.

(11) Baldwin, J. E.; Adlington, R. M.; Birch, D. J.; Crawford, J. A.; Sweeney, J. B. *J. Chem. Soc., Chem. Commun.* **1986**, 1339.

(12) Ansari, A. A.; Frejd, T.; Magnusson, G. *Carbohydr. Res.* **1987**, *161*, 225.

(13) Magnusson, G.; Lindqvist, F. *J. Chem. Soc., Chem. Commun.* **1990**, 1080.

(14) Buter, J.; Kellogg, R. M. *J. Org. Chem.* **1981**, *46*, 4481.

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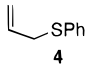
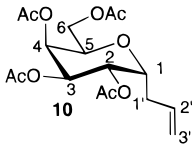
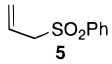
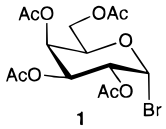
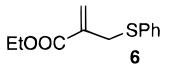
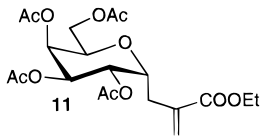
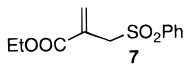
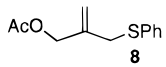
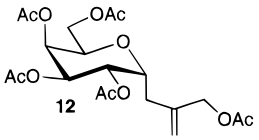
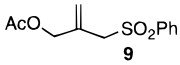
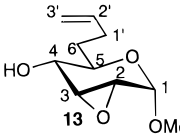
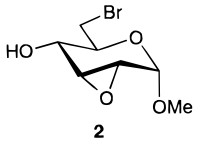
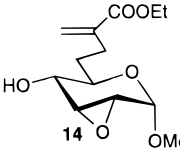
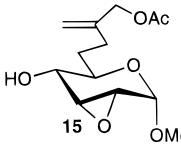
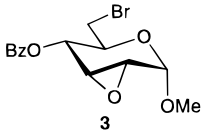
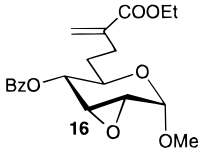
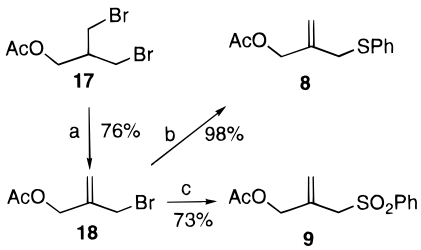
Table 1. Allylation[a] of the Bromosugars 1−3 with the Allylic Sulfides and Sulfones 4−9

Starting mtrls		Product	Yield[b] (%)
	 **4**	 **10**	73
	 **5**		87
 **1**	 **6**	 **11**	71
	 **7**		61[c]
	 **8**	 **12**	72
	 **9**		89
		 **13**	78
	4		
	5		88
 **2**	**6**	 **14**	32
	7		14
	8	 **15**	90
	9		84[d]
 **3**	**6**	 **16**	76
	7		70[e]

[a] $Bu_3SnSnBu_3$, benzene, Ar, hv. [b] Isolated product. [c] 35% of **1** was recovered. [d] 11% of **2** was recovered. [e] 21% of **3** was recovered.

Scheme 1



in C_6D_6 using C_6D_5H as internal standard (δ 7.30). ^{13}C-NMR spectra were recorded at 23 °C and 75 MHz using $CDCl_3$ or C_6D_6 as solvent and internal standard (δ 77.0 and 128.0, respectively). TLC analysis was performed on Merck SiO_2 60 F_{254} precoated aluminum sheets; spots were visualized with UV light, I_2, or by 5% anisaldehyde in ethanolic sulfuric acid. Liquid chromatography was performed on Matrex SiO_2 60 (35−70 μm). Hexabutyldistannane was purified by flash chromatography (SiO_2, heptane) and stored under argon at 4 °C. Benzene was distilled and stored over molecular sieves (4 Å). Compounds **1**,[9] **2**,[10] and **3**,[8,10] **6**,[11] **7**,[12] and **17**[13] were prepared according to the published procedures. Compounds **4** and **5** are commercially available. The naming of compounds **10**−**16** and the assignments of ^{1}H NMR spectra in the supporting information is based on the atom numbering shown for compounds **10** and **13** in Table 1.

2-[(Phenylthio)methyl]prop-2-en-1-yl Acetate (8). 2-(Bromomethyl)propen-1-ylacetate[13] (**18**, 135 mg, 0.70 mmol) was dissolved in CH_3CN (7 mL), and thiophenol (0.10 mL, 0.97 mmol) and Cs_2CO_3 (257 mg, 0.79 mmol) were added. After 20 min, **18** had been consumed (GC, RSL-150 nonpolar polydimethoxysiloxane capillary column, 60 °C). The reaction mixture was poured into water (50 mL), the water phase was extracted with diethyl ether (4 × 20 mL), and the ether solution was dried (Na_2SO_4) and concentrated. Chromatography (SiO_2, heptane/EtOAc 6:1) of the residue gave pure **8** (152 mg, 98%). ^{1}H-NMR data ($CDCl_3$): δ 7.37−7.17 (m, 5 H), 5.10 (br s, 1 H), 5.03 (br s, 1 H), 4.68 (br s, 2 H), 3.59 (br s, 2 H), 2.08 (s, 3 H). ^{13}C-NMR data ($CDCl_3$): δ 170.6, 139.3, 135.6, 130.6, 128.9, 126.7, 116.5, 65.3, 37.8, 20.9. HRMS calcd for $C_{12}H_{14}O_2S$ (M^+): 222.0715, found 222.0714.

2-[(Phenylsulfonyl)methyl]prop-2-en-1-yl Acetate (9). 2-(Bromomethyl)prop-2-en-1-yl-acetate[13] (**18**, 505 mg, 2.60 mmol) was dissolved in DMF (15 mL), and sodium benzenesulfinate (850 mg, 5.20 mmol) was added. After 15 h, the reaction mixture was poured into water (20 mL), the water

phase was extracted with ether (4 × 10 mL), and the ether solution was dried (Na_2SO_4) and concentrated. Chromatography (SiO_2, heptane/EtOAc 8:1) of the residue gave pure **9** (482 mg, 73%) as a syrup, which crystallized upon standing at −20 °C. Mp 35.5−37.5 °C; ^{1}H-NMR data ($CDCl_3$): δ 7.90 (m, 2 H), 7.53−7.70 (m, 3 H), 5.36 (br s, 1 H), 5.01 (br s, 1 H), 4.62 (br s, 2 H), 3.86 (br s, 2 H), 2.06 (s, 3 H). Anal. Calcd for $C_{12}H_{14}O_4S$: C, 56.7, H, 5.6; found: C 56.7, H, 5.5.

***C*-Propen-1-yl 2,3,4,6-Tetra-*O*-acetyl-α-D-galactopyranoside (10).** (a) Acetobromogalactose (**1**, 414 mg, 1.01 mmol) and sulfide **4** (0.44 mL, 3.00 mmol) were dissolved in dry benzene (5.5 mL). Hexabutyldistannane (0.75 mL, 1.50 mmol) was added, and the mixture was degassed by purging with Ar during sonification for 20−30 min at 15−25 °C. The flask was sealed with a rubber septum and the mixture was irradiated at rt for 5 h with a modified mercury lamp (Osram HQL 700W) equipped with a Pyrex filter. The reaction mixture was added to an SiO_2 column and chromatographed (toluene/EtOAc 1:0 → 3:1, gradient) to give **10** (272 mg, 73%) as a syrup. $[\alpha]^{23}_D$ +84° (*c* 0.9, $CHCl_3$). ^{1}H-NMR data ($CDCl_3$): δ 5.76 (dddd, 1 H, J = 6.5, 7.1, 10.0, 16.6 Hz), 5.42 (dd, 1 H, J = 2.4, 3.1 Hz), 5.28 (dd, 1 H, J = 4.8, 9.3 Hz), 5.22 (dd, 1 H, J = 3.1, 9.3 Hz), 5.13 (ddd, 1 H, J = 1.6, 3.0, 16.6 Hz), 5.12 (ddd, 1 H, J = 1.4, 3.0, 10.0 Hz), 4.30 (ddd, 1 H, J = 4.7, 5.2, 10.3 Hz), 4.21 (dd, 1 H, J = 8.9, 12.5 Hz), 4.09 (m, 2 H), 2.46 (m, 1 H), 2.29 (m, 1 H), 2.12, 2.07, 2.04, 2.03 (4 s, 3 H each). ^{13}C-NMR data ($CDCl_3$): δ 170.5, 170.1, 169.9, 169.8, 133.3, 117.6, 71.4, 68.2, 67.9, 61.4, 30.9, 20.8, 20.7, 20.6. HRMS calcd for $C_{17}H_{25}O_9$ (M + H): 373.1499; found 373.1487.

(b) Acetobromogalactose (**1**, 409 mg, 0.99 mmol) and sulfone **5** (1.189 g, 3.01 mmol) were dissolved in dry benzene (5 mL). Hexabutyldistannane (0.70 mL, 1.39 mmol) was added, and the mixture was treated as above to give **10** (322 mg, 87%) after 9 h of irradiation and purification by chromatography.

***C*-2-(Ethoxycarbonyl)prop-2-en-1-yl 2,3,4,6-Tetra-*O*-acetyl-α-D-galactopyranoside (11).** (a) Acetobromogalactose (**1**, 143 mg, 0.35 mmol) and sulfide **6** (226 mg, 1.02 mmol) were dissolved in dry benzene (2 mL). Hexabutyldistannane (0.25 mL, 0.50 mmol) was added, and the mixture was treated as in the preparation of **10** (a) to give **11** as a syrup (111 mg, 71%) after 12 h of irradiation and purification by chromatography. $[\alpha]^{23}_D$ +71° (*c* 1.3, $CHCl_3$). ^{1}H-NMR data ($CDCl_3$): δ 6.27 (d, 1 H, J = 1.0 Hz), 5.64 (d, 1 H, J = 1.0 Hz), 5.40 (dd, 1 H, J = 1.9, 3.2 Hz), 5.30 (dd, 1 H, J = 5.4, 9.8 Hz), 5.20 (dd, 1 H, J = 3.3, 9.8 Hz), 4.45 (ddd, 1 H, J = 4.8, 5.2, 10.3 Hz), 4.19 (dq, 2 H, J = 1.0, 7.1 Hz), 4.14−4.08 (m, 2 H), 4.02 (dd, 1 H, J = 8.3, 13.8 Hz), 2.63, 2.58 (dABq, 2 H, J = 4.8, 10.3, 15.2 Hz), 2.10, 2.07, 2.01, 2.00 (4 s, 12 H), 1.27 (t, 3 H, J = 7.1 Hz). ^{13}C-NMR data ($CDCl_3$): δ 170.5, 170.1, 170.0, 169.7, 166.4, 136.3, 127.5, 71.3, 68.0, 67.8, 67.6, 61.4, 60.9, 28.2, 20.8, 20.7, 20.6, 14.1. HRMS calcd for $C_{20}H_{32}O_{11}N$ (M + NH_4^+): 462.1975, found 462.1979.

(b) Acetobromogalactose (**1**, 55 mg, 0.13 mmol) and sulfone **7** (83 mg, 0.33 mmol) were dissolved in dry benzene (0.7 mL). Hexabutyldistannane (0.10 mL, 0.20 mmol) was added, and the mixture was treated as in the preparation of **10** (b) to give **11** (35 mg, 61%) and recovered **1** (19 mg, 35%) and **7** (25 mg, 30%), after 7 h of irradiation and purification by chromatography.

***C*-2-(Acetoxymethyl)prop-2-en-1-yl 2,3,4,6-Tetra-*O*-acetyl-α-D-galactopyranoside (12).** (a) Acetobromogalactose (**1**, 235 mg, 0.57 mmol) and sulfide **8** (375 mg, 1.69 mmol) were dissolved in dry benzene (3 mL). Hexabutyldistannane (0.42 mL, 0.84 mmol) was added, and the mixture was treated as in the preparation of **10** (a) to give **12** as a syrup (182 mg, 72%) after 13 h of irradiation and purification by chromatography. $[\alpha]^{23}_D$ +72° (*c* 1.6, $CHCl_3$). ^{1}H-NMR data ($CDCl_3$): δ 5.41 (dd, 1 H, J = 2.4, 2.9 Hz), 5.27 (dd, 1 H, J = 5.0, 9.3 Hz), 5.21 (dd, 1 H, J = 3.2, 9.3 Hz), 5.17 (br s, 1 H), 5.06 (br s, 1 H), 4.60, 4.52 (ABq, 2 H, J = 13.3 Hz), 4.43 (ddd, 1 H, J = 3.9, 4.9, 10.8 Hz), 4.22−4.05 (m, 3 H), 2.50 (dd, 1 H, J = 11.0, 15.4 Hz), 2.25 (dd, 1 H, J = 3.9, 15.4 Hz), 2.12, 2.08, 2.022, 2.017 (4 s, 15 H). ^{13}C-NMR data ($CDCl_3$): δ 170.5, 170.0, 169.9, 169.7, 139.7, 115.9, 70.5, 68.4, 68.2, 67.8, 67.5, 66.6, 61.3, 30.0, 20.8, 20.7, 20.6. HRMS calcd for $C_{20}H_{32}O_{11}N$ (M + NH_4^+): 462.1975, found 462.1982.

(b) Acetobromogalactose (**1**, 96 mg, 0.24 mmol) and sulfone **9** (176 mg, 0.69 mmol) were dissolved in dry benzene (1.5 mL). Hexabutyldistannane (0.18 mL, 0.35 mmol) was added, and the mixture was treated as in the preparation of **10** (b) to give **12** (93 mg, 89%) and recovered **9** (107 mg, 60%), after 7 h of irradiation and purification by chromatography.

Methyl 2,3-Anhydro-6-deoxy-6-(prop-2-en-1-yl)-α-D-allopyranoside (13). (a) Methyl 2,3-anhydro-6-bromo-6-deoxy-α-D-allopyranoside[6] (**2**, 239 mg, 1.00 mmol) and sulfide **4** (0.44 mL, 3.00 mmol) were dissolved in dry benzene (6 mL). Hexabutyldistannane (0.75 mL, 1.50 mmol) was added, and the mixture was treated as in the preparation of **10** (a) to give **13** as a syrup (157 mg, 78%) after 13 h of irradiation and purification by chromatography. $[\alpha]^{23}_D$ +116° (*c* 0.87, $CHCl_3$). ^{1}H-NMR data (C_6D_6): δ 5.95 (ddt, 1 H, J = 6.6, 10.4, 17.0 Hz), 5.20 (ddd, 1 H, J = 1.6, 3.5, 17.1 Hz), 5.13 (ddd, 1 H, J = 1.3, 3.2, 10.2 Hz), 4.54 (d, 1 H, J = 3.0 Hz), 3.75 (dt, 1 H, J = 2.4, 9.5 Hz), 3.41 (dt, 1 H, J = 1.7, 9.6 Hz), 3.30 (s, 3 H), 3.11 (dd, 1 H, J = 3.1, 4.1 Hz), 3.05 (dd, 1 H, J = 1.7, 4.1 Hz), 2.45 (m, 1 H), 2.25 (m, 1 H), 2.05 (m, 1 H), 1.60 (m, 2 H). ^{13}C-NMR data (C_6D_6): δ 138.6, 114.9, 94.9, 70.1, 68.6, 55.6, 55.2, 53.7, 31.3, 30.4. HRMS calcd for $C_{10}H_{20}O_4N$ (M + NH_4^+): 218.1392, found 218.1387.

(b) Methyl 2,3-anhydro-6-bromo-6-deoxy-α-D-allopyranoside (**2**, 33 mg, 0.14 mmol) and sulfone **5** (71 mg, 0.39 mmol) were dissolved in dry benzene (0.8 mL). Hexabutyldistannane (0.08 mL, 0.16 mmol) was added, and the mixture was treated as in the preparation of **10** (b) to give **13** (24 mg, 88%), after 17 h of irradiation and purification by chromatography.

Methyl 2,3-Anhydro-6-deoxy-6-(2-(ethoxycarbonyl)-prop-2-en-1-yl)-α-D-allopyranoside (14). (a) Methyl 2,3-anhydro-6-bromo-6-deoxy-α-D-allopyranoside[6] (**2**, 164 mg, 0.69 mmol) and sulfide **6** (445 mg, 2.00 mmol) were dissolved in dry benzene (4 mL). Hexabutyldistannane (0.50 mL, 1.00 mmol) was added, and the mixture was treated as in the preparation of **10** (a) to give **14** as a syrup (60 mg, 32%) and recovered **6** (23 mg, 14%), after 12 h of irradiation and purification by chromatography. $[\alpha]^{23}_D$ +108° (*c* 1.3, $CHCl_3$). ^{1}H-NMR data ($CDCl_3$): δ 6.15 (br s, 1 H), 5.55 (m, 1 H), 4.86 (d, 1 H, J = 3.0 Hz), 4.19 (q, 2 H, J = 7.1 Hz), 3.65 (ddd, 1 H, J = 1.7, 9.4, 9.7 Hz), 3.59−3.50 (m, 2 H), 3.46 (s, 3 H), 3.44 (dd, 1 H, J = 1.7, 4.2 Hz), 2.55 (dddd, 1 H, J = 4.5, 4.9, 10.6, 15.1 Hz), 2.30 (dddd, 1 H, J = 5.3, 6.0, 9.9, 15.2 Hz), 2.05 (dddd, 1 H, J = 2.7, 5.9, 10.7, 13.7 Hz), 1.95 (d, 1 H, J = 9.8 Hz), 1.54 (ddt, 1 H, J = 4.7, 9.6, 14.1 Hz), 1.28 (t, 3 H, J = 7.1 Hz). ^{13}C-NMR data ($CDCl_3$): δ 167.1, 142.7, 140.3, 124.7, 94.5, 69.6, 68.4, 60.7, 55.8, 54.1, 30.2, 28.1, 14.2. HRMS calcd for $C_{13}H_{24}O_6N$ (M + NH_4^+): 290.1604, found 290.1623.

(b) Methyl 2,3-anhydro-6-bromo-6-deoxy-α-D-allopyranoside (**2**, 70 mg, 0.29 mmol) and sulfone **7** (189 mg, 0.74 mmol) were dissolved in dry benzene (1.8 mL). Hexabutyldistannane (0.22 mL, 0.44 mmol) was added, and the mixture was treated as in the preparation of **10** (b) to give **14** (11 mg, 14%) and recovered **7** (125 mg, 66%), after 13 h of irradiation and purification by chromatography.

(c) Compound **16** (88 mg, 0.23 mmol) was dissolved in ethanol (99.5%, 2 mL) and ethanolic sodium ethoxide (0.1 mL, approximately 0.7 M) was added. The reaction was monitored by TLC (SiO_2, toluene/EtOAc 3:1). After 6 h, NH_4Cl(s) was added, the mixture was filtered, and the filtrate was concentrated. The residue was chromatographed (SiO_2, heptane/EtOAc 1:1) to give **14** (52 mg, 84%).

Methyl 2,3-Anhydro-6-deoxy-6-(2-(acetoxymethyl)prop-2-en-1-yl)-α-D-allopyranoside (15). (a) Methyl 2,3-anhydro-6-bromo-6-deoxy-α-D-allopyranoside[6] (**2**, 604 mg, 2.52 mmol) and sulfide **8** (1.66 g, 7.46 mmol) were dissolved in dry benzene (14 mL). Hexabutyldistannane (1.90 mL, 3.79 mmol) was added, and the mixture was treated as in the preparation of **10** (a) to give **15** as a syrup (621 mg, 90%) and recovered **8** (707 mg, 43%), after 4 h of irradiation and purification by chromatography. $[\alpha]^{23}_D$ +97° (*c* 0.56, $CHCl_3$). ^{1}H-NMR data ($CDCl_3$): δ 5.04 (br s, 1 H), 4.97 (br s, 1 H), 4.85 (d, 1 H, J = 3.2 Hz), 4.52 (s, 2 H), 3.63 (ddd, 1 H, J = 1.6, 9.3, 9.8 Hz), 3.56 (dd, 1 H, J = 3.2, 4.2 Hz), 3.52 (m, 1 H), 3.45 (s, 3 H), 3.44 (m, 1 H), 2.29 (m, 1 H), 2.08 (s, 3 H), 2.14−1.97 (m, 2 H), 1.52 (m, 1 H). ^{13}C-NMR data ($CDCl_3$): δ 170.8, 143.2, 112.6,

94.5, 69.6, 68.4, 66.8, 55.8, 55.73, 55.69, 54.1, 29.4, 20.9. HRMS calcd for $C_{13}H_{24}O_6N$ ($M + NH_4^+$): 290.1604, found 290.1606. Compound **15** was acetylated with Ac_2O and pyridine: ^{1}H-NMR data ($CDCl_3$): δ 5.06 (br s, 1 H), 4.95 (br s, 1 H), 4.87 (d, 1 H, $J = 2.4$ Hz), 4.85 (dd, 1 H, $J = 1.5, 9.3$ Hz), 4.51 (br s, 2 H), 3.82 (ddd, 1 H, $J = 2.4, 9.6, 9.7$ Hz), 3.53 (dd, 1 H, $J = 2.8, 4.2$ Hz), 3.51 (dd, 1 H, $J = 1.4, 4.2$ Hz), 3.47 (s, 3 H), 2.29 (ddd, 1 H, $J = 4.9, 5.1, 10.2$ Hz), 2.13 (s, 3 H), 2.08 (s, 3 H), 2.10−2.00 (m, 1H), 1.73 (m, 1 H), 1.50 (m, 1 H).

(b) Methyl 2,3-anhydro-6-bromo-6-deoxy-α-D-allopyranoside (**2**, 175 mg, 0.73 mmol) and sulfone **9** (466 mg, 1.83 mmol) were dissolved in dry benzene (4 mL). Hexabutyldistannane (0.55 mL, 1.10 mmol) was added, and the mixture was treated as in the preparation of **10** (b) to give **15** (167 mg, 84%) and recovered **2** (20 mg, 11%), after 13 h of irradiation and purification by chromatography.

Methyl 2,3-Anhydro-4-*O*-benzoyl-6-deoxy-6-(2-(ethoxycarbonyl)prop-2-en-1-yl)-α-D-allopyranoside (16). (a) Methyl 2,3-anhydro-4-*O*-benzoyl-6-bromo-6-deoxy-α-D-allopyranoside (**3**, 249 mg, 0.73 mmol) and sulfide **6** (487 mg, 2.19 mmol) were dissolved in dry benzene (4.1 mL). Hexabutyldistannane (0.55 mL, 1.10 mmol) was added, and the mixture was treated as in the preparation of **10** (a) to give **16** as a syrup (209 mg, 76%) after 4 h of irradiation and purification by chromatography. $[\alpha]^{23}_D$ +157° (*c* 1.1, $CHCl_3$). ^{1}H-NMR data ($CDCl_3$): δ 8.05 (m, 2 H), 7.58 (m, 1 H), 7.45 (m, 2 H), 6.15 (br s, 1 H), 5.52 (m, 1 H), 5.13 (dd, 1 H, $J = 1.6, 9.6$ Hz), 4.94 (d, 1 H, $J = 2.9$ Hz), 4.13 (q, 2 H, $J = 7.0$ Hz), 4.02 (dt, 1 H, $J = 2.1, 9.6$ Hz), 3.63 (dd, 1 H, $J = 1.5, 4.1$ Hz), 3.59 (dd, 1 H, $J = 3.0, 4.1$ Hz), 3.53 (s, 3 H), 2.58 (ddd, 1 H, $J = 4.6, 10.4, 14.9$ Hz), 2.33 (m, 1 H), 1.84 (m, 1 H), 1.59 (m, 1 H), 1.21 (t, 3 H, $J = 7.1$ Hz). ^{13}C-NMR data ($CDCl_3$): δ 166.9, 166.0, 140.0, 133.5, 129.8, 128.5, 124.9, 94.6, 71.4, 65.6, 60.6, 56.0, 54.8, 51.5, 30.1, 28.0, 14.1. HRMS calcd for $C_{20}H_{28}O_7N$ ($M + NH_4^+$): 394.1866, found 394.1859.

(b) Methyl 2,3-anhydro-4-*O*-benzoyl-6-bromo-6-deoxy-α-D-allopyranoside (**3**, 271 mg, 0.79 mmol) and sulfone **7** (606 mg, 2.38 mmol) were dissolved in dry benzene (4.4 mL). Hexabutyldistannane (0.60 mL, 1.20 mmol) was added, and the mixture was treated as in the preparation of **10** (b) to give **16** (208 mg, 70%) and recovered **3** (58 mg, 21%), after 11 h of irradiation and purification by chromatography.

2-(Bromomethyl)prop-2-en-1-yl Acetate (18). 3-Bromo-2-(bromomethyl)propyl acetate[12] (7.87 g, 28.7 mmol) was dissolved in a stirred solution of tetrabutylammonium fluoride in MeCN (0.194 M, 78.2 mmol, 400 mL). After 17 min, the starting material had been consumed (GC, RSL-150, nonpolar polydimethoxysiloxane capillary column, 100 °C), and an aqueous solution of calcium nitrate (400 mL, approximately 2 M) was added to quench the fluoride ions. The bulk of CH_3CN was removed, and the aqueous residue was extracted with ether (4 × 100 mL). The ether extract was dried (Na_2SO_4) and concentrated to give crude **18** (5.0 g). Distillation of the crude product gave pure **18** (4.21 g, 76%). Bp 52−56 °C/1 mmHg. ^{1}H-NMR data ($CDCl_3$): δ 5.38 (m, 1 H), 5.27 (m, 1 H), 4.71 (s, 2 H), 4.01 (d, $J = 0.8$ Hz, 2 H), 2.10 (s, 3 H). ^{13}C-NMR data ($CDCl_3$): δ 170.4, 140.2, 118.2, 64.3, 32.5, 28.8. Anal. Calcd for $C_6H_9BrO_2$: C 37.3, H 4.7. Found: C 37.4; H, 4.7.

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Supporting Information Available: ^{1}H NMR spectra and ^{1}H NMR data with peak assignments for all title compounds described in the Experimental Section (20 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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