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Metal-Catalyzed Organic Photoreactions. Titanium(IV) Chloride-Catalyzed Photoreactions of Aldohexoses

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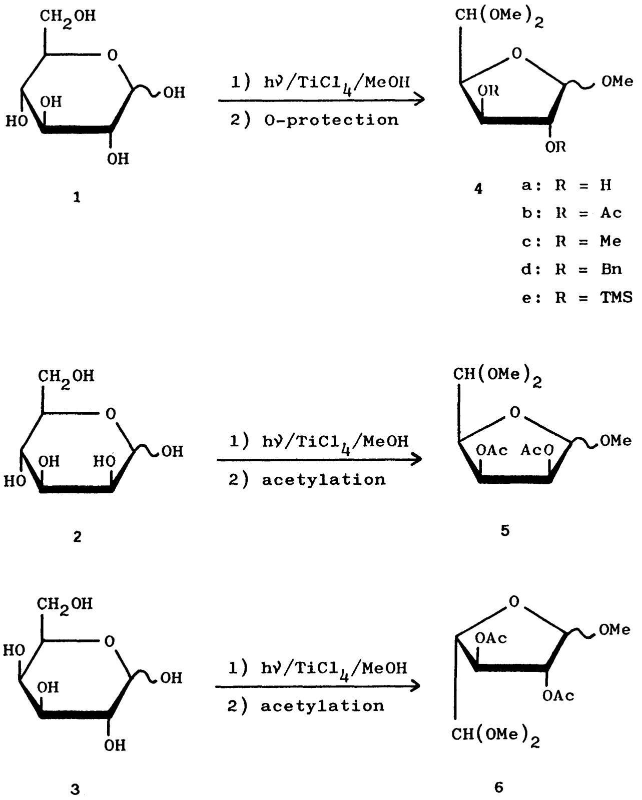
Under UV irradiation in the presence of titanium(IV) chloride in methanol, D-glucose, D-mannose, and D-galactose underwent a selective bond cleavage at the C5-C6 position, producing the corresponding pentodialdose derivatives. The reaction was interpreted in terms of the photoinduced electron transfer within a chelate of titanium ion with the carbohydrate molecule. The synthetic utilities of the photoproducts were discussed.

Although carbohydrate molecules are regarded as having either aldehyde or ketone group, the carbonyl groups are in a latent form, and they do not function as an effective chromophor to induce photoreaction. The photochemistry of the parent carbohydrate molecules has been performed either with conventional UV light (>200 nm) in the presence of molecular oxygen or sensitizers, or with shorter wavelength light (185 nm).[1] Under these conditions the reaction has been assumed to be initiated by hydroxyl radical produced from water molecule, and gives product as a mixture of various compouds. Most of the photoreactions of the carbohydrates have been carried out on derivatives having a chromophore at an appropriate position, and therefore they are regarded as the photochemistry of the chromophores, rather than that of carbohydrates themselves. Although these reactions usually proceed with high selectivity at the particular position, several steps are required to introduce the chromophore into the desired position, thus making the carbohydrate photochemistry discouraging in the synthetic chemistry field.

For some time, we have been investigating the effects of metal compounds on the photoreaction of organic molecules, and found that many photoreactions were remarkably affected by the presence of some metal compounds. One of the most unique types of reaction is the titanium(IV) chloride-catalyzed photocoupling reaction of carbonyl compounds with alcohols involving a C-C bond formation, and the reaction was applied successfully to the synthetic purpose.[2] In our previous papers,[3] we reported that D-glucose (**1**) and D-galactose (**3**), when irradiated with UV light in the presence of titanium(IV) chloride in methanol, underwent a selective cleavage of C5-C6 bond, producing pentodialdose derivatives **4** and **6**, respectively. We have schemed the reaction as involving formation of a five-membered titanium chelate with the C5, C6-diol system of the furanose form of the aldohexoses, followed by an electron transfer within the chelate.

In the present study, we irradiated D-mannose (**2**), an another aldohexose, under the same conditions, and obtained the corresponding pentodialdose derivative **5** in 50% yield. The starting carbohydrate was recovered as the corresponding methyl glycoside tetraacetate in 18% yield. Under these conditions, D-galactose was less soluble in the reacting solution, and much amount of the starting material remained unsolved even after 24 h irradiation. Although the reaction proceeded much faster when five-fold excess of titanium(IV) chloride was used, the yield of **6** was 30%, and 46% of the starting material **3** was recovered as methyl glycoside tetraacetate. The amounts of smaller fragments, which might have been derived from the carbohydrate, but of unknown structures, were also larger as compared with the other cases.

In accord with our previous observation that only the primary alcohol function was susceptible to the titanium(IV) chloride-catalyzed photoreaction,[2e] the bond cleavage at the other positions having secondary alcohol function occurred only to a minor extent, giving rise to the high selectivity of the bond cleavage at the C5-C6 position. The reaction is characteristic in that the metal compound imparts the photoreactivity to the carbohydrate molecules, which are otherwise

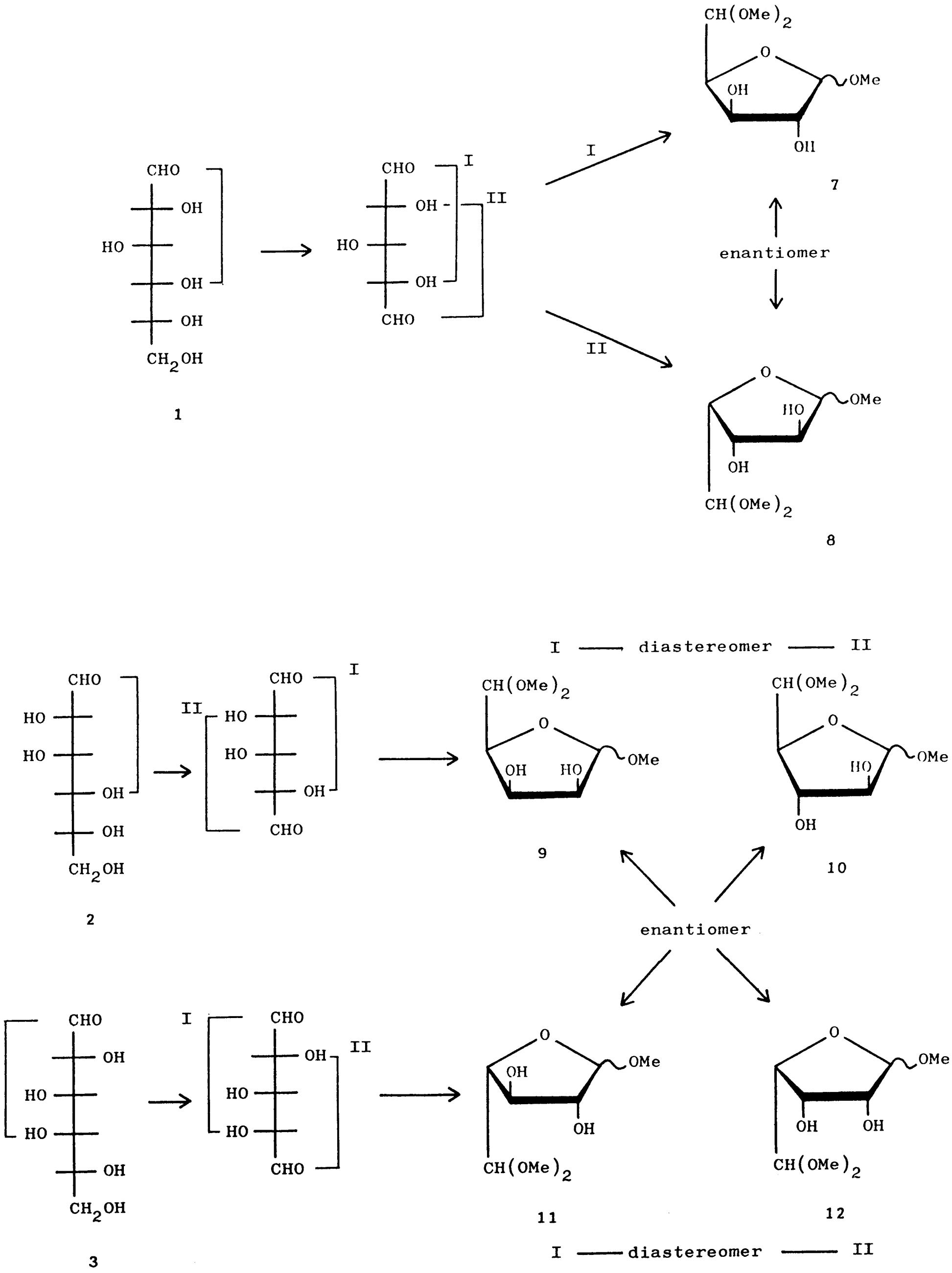


Scheme 1.

inactive towards the UV irradiation, and that the bond cleavage occurs at a specific position even without any prior protection on the carbohydrate molecules.

Since carbohydrate molecules have a series of asymmetric carbons of definite stereochemistry, they have been recognized as potential starting materials for the synthesis of chiral molecules.[4)] The drawback in using the carbohydrates for this purpose is that the reactivity of each asymmetric center is quite similar, and hence it is not an easy task to carry out a specific reaction on a specific carbon. D-Glucose has been regarded as the carbohydrate that has the widest potential applicability for the synthetic purpose. It is not only because it is inexpensive, but also because it can be easily converted to some key intermediates, in which only specific positions could be brought into reaction. Therefore, in order to develop a chemisty of carbohydrates as chiral synthons, it is essential to supply with as many key intermediates as possible in which only particular positions could be reacted. We expected that the products of the present photoreaction, pentodialdose derivatives, could serve this purpose, and explored the reaction further into detail.

Since the present reaction proceeds under Lewis acid-methanol system, there might be a possibility of ring opening, and subsequent ring closure at another aldehyde group of the dialdose derivatives, resulting in the establishment of a net equilibrium between I and II (Scheme 2). If this ring scrambling occurred, the product from D-glucose (**1**) should be a racemic mixture,



Scheme 2.

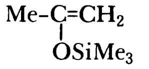
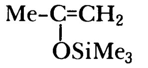
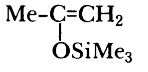
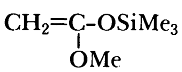
7+**8**, while the products from D-mannose (**2**) and D-galactose (**3**) should be diastereomeric mixtures of **9**+**10**, and **11**+**12**, respectively. As evident from the Scheme 2, the mixture of **9**+**10** and that of **11**+**12** should be in the enantiomeric relation of the same set of compounds. Actually, however, it was shown ^{13}C NMR and GLC analyses that the products from **2** and **3** were not identical with each other, and no traces of the enantiomeric isomers were identified. Moreover, the products from D-glucose showed optical activities as shown in the Experimental part. From these observations, we concluded that the equilibrium between I and II does not exist under the present conditions, and only **7**, **9**, and **11** were the actual products from **1**, **2**, and **3**, respectively.

Kitagawa et al.[5] have obtained pentodialdose derivatives by electrolytic oxidation of uronic acids, but, under these conditions, the ring scrambling occurred, and D-mannuronic and D-galacturonic acids gave the corresponding enantiomers of the identical compounds.

In order to evaluate the utilities of these dialdose derivatives as chiral synthons, we investigated the chemoselectivity of the two aldehyde functions and the stereoselectivity in the reactions at C5, intending to apply the photoproducts to the synthesis of polyhydroxy compounds which are furnished with definite stereochemistry and are obtainable only with difficulty by other methods.

With these intentions, we carried out the reaction of **4** with various nucleophiles in the presence of Lewis acids. The results are shown in Table 1. As evident from these results, the reaction occurred predominantly at C5, but under severer conditions, the reaction occurred also at C1. The analysis of ^{13}C NMR signals of the anomeric carbons provided us with much information concerning with the stereochemistry of the products. As shown in Table 2, all these compounds had signals at around δ 100 and 107, characteristic of the anomeric carbons having α and β configurations, respectively.[6] The signal of each region further splitted into two peaks, which we assigned to those of C5 of the corresponding diastereomers, although we could not rule out the possibility of the signal splitting due to the presence of conformers of the furanose ring. Assuming that the intensities of the signals roughly correspond to the amount of each epimers,[7] we concluded that a fair to good diastereoselectivity has been attained in the reaction at C5. Generally, better selectivity has been obtained with acetate than with methyl ethers, but obviously, the selectivity was poor with α glycoside of **17c**.

Table 1. Products and Yields of the Reaction of **4** with Nucleophiles

Substrate	Reagent	Lewis acid	Product (yield/%)
4b	$\mathrm{CH_2{=}CH\text{-}CH_2SiMe_3}$	$\mathrm{TiCl_4}$ (1 equiv)	**13b** (98)
4b	$\mathrm{CH_2{=}CH\text{-}CH_2SiMe_3}$	$\mathrm{TiCl_4}$ (4 equiv)	**21b** (88)
4b	$\mathrm{CH_2{=}CH\text{-}CH_2SiMe_3}$	TMSOTf	**20b** (60)
4c	$\mathrm{CH_2{=}CH\text{-}CH_2SiMe_3}$	TMSOTf	**13c** (98)
4d	$\mathrm{CH_2{=}CH\text{-}CH_2SiMe_3}$	TMSOTf	**13d** (60)
4b	 $\mathrm{Me\text{-}}\underset{\mathrm{OSiMe_3}}{\underset{\vert}{\mathrm{C}}}\mathrm{{=}CH_2}$	TMSOTf	**14b** (92)
4c	 $\mathrm{Me\text{-}}\underset{\mathrm{OSiMe_3}}{\underset{\vert}{\mathrm{C}}}\mathrm{{=}CH_2}$	TMSOTf	**14c** (90)
4d	 $\mathrm{Me\text{-}}\underset{\mathrm{OSiMe_3}}{\underset{\vert}{\mathrm{C}}}\mathrm{{=}CH_2}$	TMSOTf	**14d** (66)
4d	*n*-BuLi	$\mathrm{TiCl_4}$	**15d** (70)
4a	$\mathrm{LiAlH_4}$	$\mathrm{AlCl_3}$	**16c** (60)[a]
4b	$\mathrm{LiAlH_4}$	$\mathrm{AlCl_3}$	**16c** (85)[a]
4b	$\mathrm{Me_3SiCN}$	$\mathrm{TiCl_4}$	**17b** (89)
4c	$\mathrm{Me_3SiCN}$	TMSOTf	**17c** (94)
4c	 $\mathrm{CH_2{=}}\underset{\mathrm{OMe}}{\underset{\vert}{\mathrm{C}}}\mathrm{\text{-}OSiMe_3}$	TMSOTf	**18c** (82)

a) After methylation.

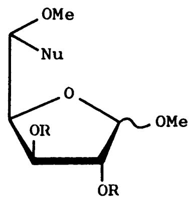
Table 2. ^{13}C NMR Signals of Anomeric Carbons[a]

Compound	δ (relative intensity)	
	α anomer	β anomer
13b	100.4 (15), 99.7 (85)	107.1 (83), 106.3 (17)
14b	100.2 (17), 99.9 (83)	107.4 (69), 107.3 (31)
14c	99.4 (30), 99.2 (70)	106.5 (73), 105.9 (27)
β-**14d**		108.3 (83), 107.2 (17)
α-**14d**	100.5 (92), 99.7 (8)	
17b	100.6 (7), 100.4 (93)	107.6 (65), 107.4 (35)
α-**17c**	108.4 (76), 107.8 (24)	
β-**17c**		101.4 (54), 100.7 (46)
19c	100.4 (29), 100.3 (71)	107.8 (72), 107.5 (28)

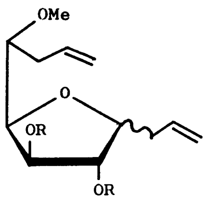
a) See footnotes 6 and 7.

When the nitrile **17c** was treated with methanol–sulfuric acid, an anomeric mixture of ester **19c** was obtained. Lithium aluminum hydride reduction of **19c**, followed by methylation gave a diastereomeric mixture of permethylated hexofuranoses. The ^{13}C NMR spectrum of the product showed two sets of signals in a relative intensity of 70 : 30, and the minor set of the spectrum was completely identical with that of **24**, prepared from 1,2 : 5,6-di-*O*-isopropylidene-D-glucose by tandem partial deprotection at C5-C6, methylation, deprotection at C1-C2, and methylation. It was concluded, therefore, that the major product was methyl tetra-*O*-methyl-L-idofuranoside **23**.

The stereoselective alkylation of aldehyde **25** to produce 6-deoxyhexose derivatives **26** has been reported, and the reaction proceeds with chelating or non-chelating intermediate depending upon the reaction conditions.[8] However, all attempts at the preparation of hexose derivatives from **25** have been achieved only without any appreciable stereoselectivity.[9] It was found that the diastereoselectivity in the nucleophilic substitution at C5 of **4** stayed around 70 : 30, irrespective of the protective groups in **4** and the reaction conditions. The selectivity was also the same between allylation and acetonylation, since the Wacker oxidation of **13b** gave the same set of the diastereomers as



Nu:
13: $CH_2CH{=}CH_2$
14: CH_2COMe
15: n-Bu
16: H
17: CN
18: CH_2COOMe
19: COOMe



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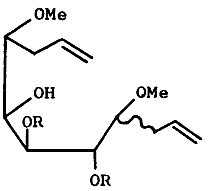

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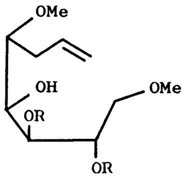

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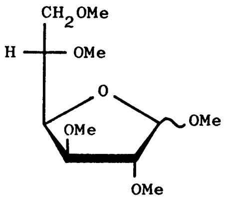
a: R = H; b: R = Ac; c: R = Me;
d: R = Bn; e: R = TMS



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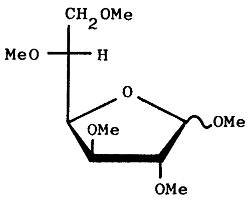

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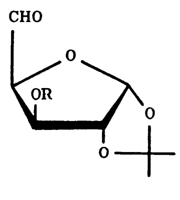

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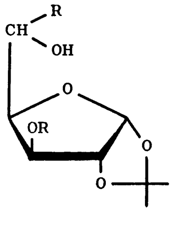

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that obtained by the direct acetonylation of **4b**. Since we can prepare **4** from D-glucose in only two steps of photoreaction and methylation, the achievement of the higher selectivity could be very useful for setting up the configuration of L-idose system.

When the reduction product **16a** was methylated, it gave permethylated D-xylofuranoside **16c** in 85% yield, which was identical with the compound obtained in minor amount (12%) by the methylation of D-xylose. Since the methylation of D-xylose gave the permethylated product mostly in pyranoside form (85%), the present reaction could be a synthetic method for D-xylofuranoside derivatives. Lithium aluminum hydride reduction of **13c** gave an open chain compound **22c**. The products of the types of **21** and **22** are also promising as chiral synthons, because they have three different types of hydroxyl function of definite stereochemistry: One is unprotected, and the other two have two different protective groups from each other.

Since the preparation of the aldehydes corresponding to **25** from D-mannose and D-galactose in conventional manners are much more difficult as compared with the case from D-glucose, the manipulation of **2** and **3** would lead to an important development of the chemistry from these carbohydrates as chiral synthons.

Experimental

General Procedures and Instrumentation. GLC experiments were carried out on a 2.5 m×3 mm stainless steel column packed with Silicone SE30 or Carbowax 20M on silanized Chromosorb W. Preparative TLC was carried out on silica-gel plates using solvents as indicated. Unless otherwise stated, all the spectroscopic data were determined on a pure sample obtained by either distillation, preparative TLC, or column chromatography. ^{1}H NMR spectra (60 MHz) were recorded on a Hitachi R-24 or JEOL PMX 60SI spectrometer. ^{1}H NMR (90 MHz) and ^{13}C NMR spectra were measured on a Hitachi R-90H spectrometer. GC-MS spectra were taken on a Shimadzu QP-1000 mass spectrometer, and high-resolution mass spectra on a JEOL DX-300 mass spectrometer. UV spectra were measured on a Shimadzu UV-240 spectrometer.

All the irradiations were carried out using a high-pressure mercury lamp [Ushio UM 452 (450 W) or Sen HL-1000 (1 kW)] at the temperature of running water.

We tried several methods for the product isolation including column chromatography or HPLC, and found that distillation under the reduced pressure was the most convenient technique without appreciable difference in the product composition. Therefore we used the technique in most of the experiments.

Titanium(IV) Chloride-Catalyzed Photoreaction of D-Glucose (1). D-Glucose (2.0 g, 11.1 mmol) was dissolved in methanol (200 ml) containing $TiCl_4$ (1.5 ml, 13.8 mmol), and the solution was irradiated with a 1 kW lamp in a quartz vessel for 24 h. The solution was neutralized with 4 M NaOHaq (1M=1 mol dm^{-3}), and the precipitates of titanium hydroxide were filtered off. The filtrate was concentrated to dryness, and the residue was vigorously shaken with ethyl acetate several times. The solvent was removed in vacuo from the extract, and the residue was distilled under reduced pressure. After some amount of forerun (0.21 g), the main fraction was obtained as a viscous oil (1.4 g), bp 89—90 °C (0.07 mmHg (1 mmHg=133.322 Pa)). Although the purity of the distillate could not be analyzed by GLC or TLC, the oil proved to be mainly **4a**, in view of the following results.

Acetylation: The crude **4a** (355 mg) was treated with acetic anhydride (1.4 ml) in pyridine (4.3 ml) for 18 h. Distillation with a Kugelrohr gave a main fraction as a viscous oil (288 mg), bp 150—170 °C (1 mmHg). GLC analysis showed that the fraction contained 85% of **4b**. Further distillation gave a pure sample of **4b**, which was shown to be a mixture of α and β anomers by GLC analysis. β Anomer was isolated in pure state by a preparative GLC, while α anomer was not completely freed from the β anomer. For β-**4b**: GC-MS, m/z (rel intensity) 261 (M^+—OMe, 0.5), 201 (0.3), 159 (4.0), 87 (10.4), 75 (100). ^{1}H NMR (CCl_4), δ=2.14 and 2.16 (6H, s×2, Ac), 3.39, 3.43, and 3.47 (9H, s×3, OMe), 4.21 (1H, dd, $J_{4,3}$=5.8 Hz, $J_{4,5}$=7.6 Hz, H_4), 4.47 (1H, d, $J_{5,4}$=7.6 Hz, H_5), 4.71 (1H, s, H_1), 4.90 (1H, br s, H_2), 5.26 (1H, br, d, $J_{3,4}$=5.8 Hz, H_3). ^{13}C NMR ($CDCl_3$), δ=169.4 (Ac-CO), 107.3 (C_1), 102.1 (C_5), 80.7 (C_4), 78.9 (C_2), 74.4 (C_3), 55.6, 54.5, and 53.0 (OMe), 20.8 and 20.6 (Ac-Me). IR 1738 (AcO), 1221 cm^{-1} (C-O). $[\alpha]_D^{24}$=+2.9 (c 0.05, $CHCl_3$). Found: C, 50.04; H, 6.68%. Calcd for $C_{12}H_{20}O_8$: C, 49.31; H, 6.90%. For α-**4b** (obtained by subtracting the data of β anomer from those of the mixture): GC-MS: same as that of the β anomer. ^{1}H NMR (CCl_4), δ=2.13—2.18 (6H, singlets, Ac), 3.39—3.44 (9H, singlets, OMe), 4.16—4.19 (2H, m, H_4, H_5), 4.79 (1H, br s, H_2), 4.96 (1H, d, $J_{1,2}$=4.5 Hz, H_1), 5.37 (1H, br d, $J_{3,4}$=6.0 Hz, H_3). ^{13}C NMR ($CDCl_3$), δ=169.6 (Ac-CO), 101.4 (C_1), 100.4 (C_5), 77.6 (C_4), 74.5 (C_2), 73.9 (C_3), 55.8, 54.5, and 53.0 (OMe), 20.8 and 20.6 (Ac-Me).

Methylation: Sodium hydride (350 mg, 14.6 mmol) was added to a solution of **4a** (400 mg, 1.9 mmol) in tetrahydrofuran, and the mixture was stirred for 30 min at room temperature. Methyl iodide (1.0 ml, 15 mmol) was added, and the solution was stirred for 20 h. After the addition of methanol, the solution was concentrated to dryness, and ice-water was added. The product was extracted with $CHCl_3$, dried over $MgSO_4$, and the distillation gave **4c** (358 mg), bp 110 °C (0.7 mmHg). GLC analysis showed two peaks corresponding to α and β anomers. Each anomer was separated on a preparative TLC (hexane/ether=1/2). For α-**4c**: GC-MS, m/z (rel intensity) 205 (M^+—OMe, 0.3), 173 (0.4), 161 (1.1), 145 (0.5), 130 (0.8), 75 (100). ^{1}H NMR ($CDCl_3$), δ=3.38, 3.43, 3.44, 3.46, and 3.50 (15H, s×5, OMe), 3.73—4.00 (2H, m, H_2, H_3), 4.20 (1H, t, $J_{4,3}$=$J_{4,5}$=6.3 Hz, H_4), 4.54 (1H, d, $J_{5,4}$=6.3 Hz, H_5), 4.99 (1H, d, $J_{1,2}$=4.5 Hz, H_1). ^{13}C NMR ($CDCl_3$), δ=101.8 (C_1), 101.0 (C_5), 85.7 (C_2), 83.8 (C_3), 77.2 (C_4), 58.5, 58.4, 55.5, 55.2, and 52.8 (OMe). $[\alpha]_D^{24}$=−1.2 (c 0.01, $CHCl_3$). For β-**4c**: GC-MS, same as that of the α anomer. ^{1}H NMR ($CDCl_3$), δ=3.38, 3.40, 3.43, 3.44, 3.47 (15H, s×5, OMe), 3.67—3.75 (2H, br, H_2, H_3), 4.09 (1H, dd, $J_{4,3}$=5.3 Hz, $J_{4,5}$=7.9 Hz, H_4), 4.57 (1H, d, $J_{5,4}$=7.9 Hz, H_5), 4.84 (1H, s, H_1). ^{13}C NMR ($CDCl_3$), δ=108.0 (C_1), 102.9 (C_5), 87.7 (C_2), 83.3 (C_3), 80.1 (C_4), 58.1, 57.3, 55.6, 55.4, and 53.1 (OMe). $[\alpha]_D^{25}$=+5.5 (c 0.013, $CHCl_3$).

Benzylation: The benzylation was carried out in the same way as for the methylation described above. The product **4d** was obtained through preparative TLC as an anomeric mixture (α/β=1/9) in 56% yield. For β-**4d**: ^{1}H NMR (CCl_4), δ=3.27—3.36 (9H, s×3, OMe), 3.88 (1H, br s, H_2), 3.91—4.25 (2H, m, H_3, H_4), 4.57 (1H, d, $J_{5,4}$=7.8 Hz, H_5), 4.79 (1H, s, H_1), 4.40 and 4.45 (4H, s×2, Ar-CH_2), 7.25 (10H, s, Ar). ^{13}C NMR ($CDCl_3$), δ=142.2—127.8 (Ar), 108.3 (C_1), 102.6 (C_5), 86.4 (C_2), 81.3 (C_3), 80.3 (C_4), 72.6 and 72.0 (Ar-CH_2), 55.6, 55.1, and 53.0 (OMe). For α-**4d** (obtained by subtracting the data of β anomer from those of the mixture): ^{13}C NMR ($CDCl_3$), δ=101.8 (C_1), 101.0 (C_5), 83.8 (C_2), 82.4 (C_3), 76.0 (C_4), 59.7, 59.3, and 57.0 (OMe).

Trimethylsilylation: The silylation was carried out using **4a** (620 mg, 3.0 mmol), hexamethyldisilazane (3 ml, 24 mmol), and chlorotrimethylsilane (0.4 ml, 4.4 mmol) in tetrahydrofuran (55 ml) by stirring at room temperature for 43 h. The product **4e** (1.028 g, 98% yield) was obtained in pure state by distillation, bp 190 °C (20 mmHg). For **4e** (as an anomeric mixture): GC-MS, m/z (rel intensity) 321 (M^+—OMe, 0.3), 305 (0.3), 247 (1.1), 231 (1.2), 217 (39.3), 133 (24.9), 75 (100), 73 (41.3). ^{1}H NMR (CCl_4), δ=0.04 (18H, s, TMS), 3.20—3.35 (9H, singlets, OMe), 3.68—4.09 (3H, m, H_2, H_3, H_4), 4.21—4.73 (2H, m, H_1, H_5). ^{13}C NMR ($CDCl_3$), δ=110.7 (β-C_1), 102.5 (α-C_1), 102.7 (β-C_5), 101.9 (α-C_5), 80.3 (β-C_4), 76.8 (α-C_4), 82.1, 78.4, 77.2, and 76.1 (C_2, C_3), 55.5, 54.6, 54.5, 53.0, and 52.6 (OMe), 5.26 (TMS). $[\alpha]_D^{25}$=+0.83 (c 0.380, $CHCl_3$).

Titanium(IV) Chloride-Catalyzed Photoreaction of D-Mannose (2). Under the same conditions as for D-glucose, the product **5** was obtained in 50% yield. For **5** (as an anomeric mixture): GC-MS, m/z (rel intensity) 261 (M^+—OMe, 0.4), 201 (1.6), 169 (3.4), 159 (3.0), 126 (7.1), 115 (3.3), 99 (4.3), 87 (11.0), 75 (100). ^{1}H NMR (CCl_4), δ=2.01—2.16 (6H, singlets, Ac), 3.35—3.41 (9H, singlets, OMe), 3.82—4.61 (3H, m, H_1, H_4, H_5), 4.75—5.19 (2H, m, H_2, H_3). ^{13}C NMR ($CDCl_3$), δ=170.3—169.5 (Ar-CO), 106.9 (α-C_1), 103.4 (β-C_1), 105.1 (α-C_5), 101.5 (β-C_5), 81.5 and 80.9 (C_4), 78.7 and 77.4 (C_2), 76.0 and 75.4 (C_3), 55.7—53.1 (OMe), 23.2 (Ac-Me). $[\alpha]_D{}^{27}$=+8.6 (c 0.070, $CHCl_3$). HRMS: Found: m/z 261.0984. Calcd for $C_{11}H_{17}O_7$ (M^+—OMe): 261.0974.

Titanium(IV) Chloride-Catalyzed Photoreaction of D-Galactose (3). The photoreaction was carried out using D-galactose (2.0 g, 11.1 mmol) and $TiCl_4$ (6.0 ml, 55.6 mmol) in methanol (200 ml) in the same way as above to produce **6** in 30% yield. For **6** (as an anomeric mixture): GC-MS, m/z (rel intensity) 261 (M^+—OMe, 1.9), 201 (1.6), 169 (3.4), 158 (4.6), 126 (9.8), 115 (3.3), 99 (5.3), 87 (14.0), 75 (100). ^{1}H NMR (CCl_4), δ=1.96—2.11 (6H, singlets, Ac), 3.27—3.41 (9H, singlets, OMe), 3.78—4.39 (3H, m, H_1, H_2, H_5), 4.72—5.14 (2H, m, H_2, H_3). ^{13}C NMR ($CDCl_3$), δ=170.3—168.8 (Ac-CO), 107.2 (α-C_1), 100.8 (β-C_1), 99.8 (α-C_5), 95.9 (β-C_5), 81.3 and 80.3 (C_4), 78.0 and 77.2 (C_2), 76.8 and 75.4 (C_3), 55.1—54.1 (OMe), 20.8 (Ac-Me). HRMS: Found: m/z 261.0985. Calcd for $C_{11}H_{17}O_7$ (M^+—OMe): 261.0974.

Titanium(IV) Chloride-Catalyzed Allylation of 4b. To a solution of **4b** (0.129 g, 0.33 mmol) in CH_2Cl_2 (4.7 ml) was added allyltrimethylsilane (0.16 ml, 1.0 mmol) and then a solution of $TiCl_4$ (0.127 g, 0.67 mmol) in CH_2Cl_2 (0.3 ml) at room temperature. The solution was stirred for 10 min at room temperature, added to cold water, and extracted with ether. The extract was washed with water and dried over Na_2SO_4. Evaporation of the solvent gave an oil, 0.104 g, which proved to be a mixture of **13b** (97%) and **4b** (2.5%) by GLC analysis. Pure sample of **13b** was obtained by a preparative TLC (ether/$CHCl_3$=1/9). For **13b** (as an anomeric mixture): GC-MS, m/z (rel intensity) 271 (M^+—OMe, 0.5), 261 (2.4), 217 (1.3), 201 (2.4), 159 (11.3), 126 (9.9), 115 (17.9), 85 (33.6), 43 (100). ^{1}H NMR (CCl_4), δ=2.02—2.13 (6H, singlets, Ac), 2.20—2.49 (2H, m, -$\underline{CH_2}$CH=CH_2), 3.35—3.53 (6H, singlets, OMe), 3.91—4.27 (2H, m, H_4, H_5), 4.61—5.22 (5H, m, H_1, H_2, H_3, -CH=C$\underline{H_2}$), 5.37—6.18 (1H, m,

$-C\underline{H}=CH_2$). ^{13}C NMR ($CDCl_3$), δ=170.2, 170.1, 169.7, and 169.2 (Ac-CO), 134.2 and 134.0 ($-\underline{C}H=CH_2$), 117.6 and 117.2 ($-CH=\underline{C}H_2$), 107.1 and 106.3 (83 : 17) (R-C_1), 100.4 and 99.7 (15 : 85) (S-C_1), 82.9 and 80.0 (C_4), 79.9 and 78.5 (C_5), 76.9 and 76.3 (C_2), 75.1 and 74.4 (C_3), 58.8, 57.9, 55.9, and 55.5 (OMe), 35.3 and 34.8 ($-\underline{C}H_2-CH=CH_2$), 20.8, 20.7, and 20.6 (Ac-Me).

When the reaction was carried out with larger amount of the Lewis acid, using **4b** (0.120 g, 0.33 mmol), $TiCl_4$ (0.15 ml, 1.33 mmol), and allyltrimethylsilane (0.21 ml, 1.33 mmol) under the otherwise same conditions as above, the product was **21b**, which was obtained in pure state on a column chromatography. For **21b** (as an anomeric mixture): GC-MS, *m/z* (rel intensity) 303 (M^+—OMe, 0.7), 271 (1.0), 183 (1.0), 169 (1.5), 137 (1.8), 85 (71.6), 55 (21.4), 43 (100). ^{1}H NMR (CCl_4), δ=1.95—2.11 (6H, singlets, Ac), 2.19—2.35 (4H, m, $-C\underline{H}_2-CH=CH_2\times2$), 3.35 (6H, singlets, OMe), 3.11—3.68 (3H, m, H_1, H_4, H_5), 4.66—5.30 (6H, m, H_2, H_3, $C\underline{H}_2=CH-\times2$), 5.44—6.13 (2H, m, $CH_2=C\underline{H}-\times2$). ^{13}C NMR ($CDCl_3$), δ=175.0—172.7 (Ac-CO), 134.0—133.6, 118.1—117.4, and 35.1—33.7 (allyls), 80.0, 79.6, 79.1, and 78.9 (C_1, C_5), 74.1 and 72.8 (C_4), 71.8, 71.7, 76.0, and 69.1 (C_2, C_3), 20.9 (Ac-Me). IR (neat), ν_{max} 3550 (OH), 1740 (acetate), 1650 cm^{-1} (olefin). Found: C, 58.12; H, 7.98%. Calcd for $C_{17}H_{28}O_7$: C, 59.28; H, 8.19%.

Trimethylsilyl Triflate-Catalyzed Allylation of 4b. A mixture of **4b** (0.12 g, 0.41 mmol), allyltrimethylsilane (0.16 ml, 1 mmol), and TMSOTf (22.2 mg, 0.1 mmol) in acetonitrile (2 ml) was stirred for 30 min. The solution was added to Na_2CO_3aq, and extracted with ether. After drying over Na_2SO_4, ether was evaporated to give **13b** (0.125 g, 100% yield) as a single product.

When the reaction time was prolonged to 46 h, or when the solution was refluxed for 1 h, in the above reaction, the crude product remained after the evaporation of ether showed two spots on a TLC. Separation on a preparative TLC gave a diallyl compound **20b** (48 mg, 60% yield) as well as the monoallyl compound **13b** (35 mg, 35% yield). For **20b** (as C_1, C_5-diastereomeric mixture): GC-MS, *m/z* (rel intensity) 281 (M^+—OMe, 0.16), 271 (3.1), 211 (3.0), 169 (8.4), 137 (14.0), 125 (10.3), 109 (10.2), 85 (54.3), 43 (100). ^{1}H NMR (CCl_4), δ=2.02 and 2.05 (6H, s×2, Ac), 2.10—2.40 (4H, m, $-C\underline{H}_2-CH=CH_2\times2$), 3.28 and 3.32 (6H, s×2, OMe), 3.04—4.32 (3H, m, H_1, H_4, H_5), 4.61—5.22 (6H, m, H_2, H_3, $C\underline{H}_2=CH-\times2$), 5.31—6.11 (2H, m, $CH_2=C\underline{H}-\times2$). ^{13}C NMR ($CDCl_3$), δ=169.6 and 169.5 (Ac-CO), 134.2—133.8, 117.4—117.1, and 35.1, 33.9 (allyls), 82.9, 82.2, 80.5, 80.3, 79.5, 79.0, 78.7, 76.7 (C_1—C_5), 58.5 and 58.3 (OMe), 20.9 and 20.8 (Ac-Me).

Acetonylation of 4b, 4c, 4d. 2-(Trimethylsilyloxy)-1-propene (0.16 ml, 1 mmol) was added to a solution of **7b** (0.1 g, 0.34 mmol) in acetonitrile (3 ml), and the solution was cooled to 0 °C. To the solution was added TMSOTf (0.01 ml, 0.05 mmol), and stirred for 20 min at 0 °C. The conventional workup produced crude **14b**, 106 mg. Pure sample was obtained by a preparative TLC. In the same way, methyl (**14c**) and benzyl (**14d**) derivatives were obtained. A preparative TLC of **14d** gave pure sample of (R)-C_1 anomer. For **14b** (as an anomeric mixture): GC-MS, *m/z* (rel intensity) 243 (M^+—Me—AcOH, 0.1), 217 (1.9), 183 (0.3), 158 (1.0), 157 (1.4), 153 (0.9), 115 (13.6), 101 (3.9), 87 (5.0), 43 (100). ^{1}H NMR (CCl_4), δ=1.98—2.13 (9H, singlets, AcO and Ac), 2.31—2.75 (2H, m, $AcCH_2-$), 3.19—3.40 (6H, singlets, OMe), 3.52—4.27 (2H, m, H_4, H_5), 4.65—5.59 (3H, m, H_1, H_2, H_3). ^{13}C NMR ($CDCl_3$), δ=206.6—205.8 (acetonyl-CO), 170.2—169.2 (Ac-CO), 107.4 and 107.3 (69 : 31, (R)-C_1), 100.2 and 99.9 (17 : 83, (S)-C_1), 82.7—74.2 (C_2—C_5), 59.3—55.2 (OMe), 46.1—44.3 (acetonyl-CH_2), 31.1—30.9 (acetonyl-Me), 20.7 and 20.6 (Ac-Me). For **14c** (as an anomeric mixture): GC-MS, *m/z* (rel intensity) 231 (M^+—OMe, 13.3), 204 (25.3), 161 (2.5), 101 (100), 88 (17.1), 75 (40.6), 73 (20.8), 45 (20.0), 43 (37.5). ^{1}H NMR (CCl_4), δ=2.12 (3H, s, acetonyl-Me), 2.43—2.61 (2H, m, acetonyl-CH_2), 3.31—3.47 (12H, singlets, OMe), 3.47—4.05 (4H, m, H_2, H_3, H_4, H_5), 4.55—4.82 (1H, m, H_1). ^{13}C NMR ($CDCl_3$), δ=209.2—207.9 (acetonyl-CO), 106.5 and 105.9 (73 : 27, (R)-C_1), 99.4 and 99.2 (30:70, (S)-C_1), 86.8—80.8 (C_2-C_5), 57.7—53.1 (OMe), 45.1—41.8 (acetonyl-CH_2), 30.5—27.6 (acetonyl-Me). For 1(R)-**14d**: ^{1}H NMR (CCl_4), δ=2.01—2.12 (3H, singlets, acetonyl-Me), 2.41—2.73 (2H, m, acetonyl-CH_2), 3.22—3.39 (6H, singlets, OMe), 3.73—4.17 (4H, m, H_2-H_5), 4.48 (4H, s, benzyl-$CH_2\times2$), 4.87 (1H, d, $J_{1,2}$=7.9 Hz, H_1) 7.25 (10H, s, Ar×2). ^{13}C NMR ($CDCl_3$), δ=207.1 (acetonyl-CO), 108.3 and 107.2 (83 : 17, C_1), 85.8—75.4 (C_2—C_5), 58.6, 57.6, 55.9, and 54.8 (OMe), 46.8 and 46.2 (acetonyl-CH_2), 30.8 and 28.9 (acetonyl-Me), 72.0, 71.9, 139.7—126.7 (benzyl). For 1(S)-**14d** (obtained by subtracting the data of (R) anomer from those of mixture), ^{1}H NMR (CCl_4), δ=2.01—2.25 (3H, singlets, acetonyl-Me), 2.35—2.92 (2H, m, acetonyl-CH_2), 3.38—3.47 (6H, singlets, OMe), 3.78—4.23 (4H, m, H_2-H_5), 4.51 (4H, m, benzyl-CH_2), 4.81—4.97 (1H, m, H_1), 7.30 (10H, s, Ar). ^{13}C NMR ($CDCl_3$), δ=206.7 (acetonyl-CO), 100.5 and 99.7 (92 : 8, C_1), 84.9—74.9 (C_2—C_5), 58.1 and 55.0 (OMe), 45.1 and 44.9 (acetonyl-CH_2), 30.4 and 30.3 (acetonyl-Me), 72.0, 71.9, 137.8—127.5 (benzyl).

Methyl D-Xylofuranoside Trimethyl Ether 16c. A suspension of $AlCl_3$ (266 mg, 2 mmol) in ether (1 ml) was stirred at 0 °C for 30 min. To the mixture was added a slurry of LAH (26 mg, 0.67 mmol) in ether (1 ml), and stirred for 30 min. A solution of **4b** (100 mg, 0.34 mmol) in ether (1 ml) was added and stirred for 2 h at room temperature. The reaction mixture was quenched by adding 10% H_2SO_4aq and then neutralized with dil NaOHaq. The solid material was filtered off, and the filtrate was concentrated in vacuo to produce an oil. Upon methylation with MeI and NaH, the oil gave **16c** in 85% yield. This was identical (GC-MS) with the sample prepared by methylation of D-xylose in the same way as above.

Cyanation of 4b and 4c. To a solution of **4c** (80 mg, 0.33 mmol) in acetonitrile (3 ml) was added TMSCN (0.14 ml, 1 mmol) and TMSOTf (0.01 ml, 0.05 mmol), and the solution was stirred for 2.5 h at room temperature. After the reaction, 10% Na_2CO_3aq (10 ml) was added and extracted with ether. The extract was dried over Na_2SO_4, and the solvent was removed to give an oil (78 mg). Pure sample of **17c** (69 mg) was obtained by the bulb-to-bulb distillation. bp 115 °C (0.1 mmHg). A preparative TLC of **17c** gave pure sample of (S)-C_1 anomer. In the same way, the acetate **17b** was obtained from **4b** in 87% yield. Bp 120 °C (0.03 mmHg). The same compound was also obtained from **4b** using $TiCl_4$ as a Lewis acid in CH_2Cl_2 in 89% yield. For 1(S)-**17c**: GC-MS, *m/z* (rel intensity) 200 (M^+—OMe, 0.1), 161 (4.1), 149 (2.0), 140 (1.2), 129 (2.9), 101 (100), 88 (6.8), 75 (70.4). ^{1}H NMR ($CDCl_3$), δ=3.46—3.54 (12H, singlets, OMe), 3.29—4.49 (4H, m, H_2-H_5), [5.05 (1/2H, d, $J_{1,2}$=3.9 Hz) and 5.07 (1/2H, d, $J'_{1,2}$=3.9 Hz), H_1]. ^{13}C NMR ($CDCl_3$), δ=116.3 (CN), 101.4 and 100.7 (1 : 1, C_1), 85.2 and 85.1 (C_2), 83.0 and 82.2 (C_3), 76.6 and 76.4 (C_4), 70.8 and 69.9 (C_1), 58.8—55.8 (OMe). For

1(R)-**17c** (obtained by subtracting the data of 1-(S) anomer from those of mixture): ^{1}H NMR ($CDCl_3$), δ=3.36—3.55 (12H, singlets, OMe), 3.71—4.55 (4H, m, H_2-H_5), 4.85 (1/5H, s, H_1), 4.91 (4/5H, s, H_1). ^{13}C NMR ($CDCl_3$), δ=117.2 and 116.4 (19:81, CN), 108.4 and 107.8 (76:24, C_1), 87.6 and 87.0 (C_2), 84.9 and 83.1 (C_3), 80.7 and 79.4 (C_4), 71.1 and 70.4 (C_5), 59.1—55.5 (OMe). For **17b** (as a diastereomeric mixture): GC-MS, *m/z* (rel intensity) 256 (M^+—OMe, 3.1), 217 (7.0), 157 (30.6), 154 (14.2), 129 (18.5), 115 (100), 87 (43.3). ^{1}H NMR (CCl_4), δ=2.02—2.15 (6H, singlets, Ac), 3.37—3.49 (6H, singlets, OMe), 4.02—4.61 (2H, m, H_4, H_5), 4.72—5.76 (3H, m, H_1, H_2, H_3). ^{13}C NMR ($CDCl_3$), δ=170.0—168.9 (Ac-CO), 116.3—115.4 (CN), 107.6 and 107.4 (65:35, (R)-C_1), 100.6 and 100.4 (7:93, (S)-C_1), 80.5—73.5 (C_2, C_3, C_5), 70.5—69.7 (C_4), 58.5—55.6 (OMe), 20.6—20.3 (Ac-Me).

Methanolysis of the Nitrile 17c. To a solution of **17c** (115 mg, 0.5 mmol) in methanol (5 ml) was added 98% H_2SO_4 (1.5 ml). The solution was kept at room temperature for 24 h, and poured into water. The solution was shaken with $CHCl_3$, and the extract was dried over Na_2SO_4. Evaporation of the solvent gave an oil **19c**, 120 mg. Bulb-to-bulb distillation gave pure sample, 116 mg. Bp 120 °C (0.1 mmHg). For **19c** (as an anomeric mixture): GC-MS, *m/z* (rel intensity) 205 (M^+—COOMe, 48.5), 161 (20.3), 145 (11.2), 129 (10.2), 101 (100), 75 (42.6). ^{1}H NMR ($CDCl_3$), δ=3.18—3.52 (12H, singlets, OMe), 3.76—3.83 (3H, singlets, COOMe), 3.86—4.16 (3H, m, H_2, H_3, H_4), 4.46—4.63 (1H, m, H_5), [4.85 (3/20H, d, δ=0.9 Hz) and 4.89 (7/20H, d, J=0.9 Hz), H_1 of 1(R) anomer], 4.97 (1/2H, d, J=3.5 Hz, H_1 of 1(S) anomer). ^{13}C NMR ($CDCl_3$), δ=171.4—170.1 (ester-CO), 107.8 and 107.5 (72:28, (R)-C_1), 100.4 and 100.3 (29:71, (S)-C_1), 89.5—76.6 (C_2—C_5), 58.8—54.9 (OMe), 52.6—51.2 (ester-Me). Found: C, 49.99; H, 7.63%. Calcd for $C_{11}H_{20}O_7$: C, 50.45; H, 7.51%.

Methyl L-Idofuranoside Tetramethyl Ether 23. To a solution of **19c** (90 mg, 0.33 mmol) in dry ether (5 ml) was added LAH (39 mg, 1 mmol), and stirred for 2 h at room temperature. Methanol and then 4 M HClaq were added to quench the excess LAH, and the solution was neutralized with 10% NaOHaq. The solid material was filtered off, and the filtrate was concentrated to dryness in vacuo. The remaining material was triturated with dry THF, and washed NaH (50 mg, 2.1 mmol) was added. After the mixture was stirred for 30 min, methyl iodide (1.6 ml, 5 mmol) was added, and the mixture was stirred for 18 h at room temperature. The excess NaH was quenched by addition of methanol, and the solution was concentrated in vacuo. The remaining material was dissolved in water, and extracted with $CHCl_3$. The extract was dried over Na_2SO_4, and the solvent was removed in vacuo. The crude material (84 mg), showing only one peak on a GLC analysis, was distilled to give an oil (77 mg). The ^{13}C NMR of the oil showed two sets of the signals in a ratio of 25:75. The set of the minor signals completely coincided with those of **24**, obtained in a way described below. The data of **23** were obtained by subtracting the data of **24** from those of the mixture oil. For **23**: GC-MS, *m/z* (rel intensity) 205 (M^+—CH_2OMe, 0.4), 173 (1.2), 161 (7.0), 145 (5.0), 101 (100), 75 (58.5), 59 (15.5), 45 (63.4). ^{1}H NMR ($CDCl_3$), δ=3.39—3.57 (15H, singlets, OMe), 3.60—4.36 (6H, m, H_2-H_6), 4.90 (1/2H, d, J=1.1 Hz, H_1 of α anomer (1R)), 4.95 (1/2H, d, J=3.0 Hz, H_1 of β anomer (1S)). ^{13}C NMR ($CDCl_3$), δ=108.1 (C_1 of α anomer), 100.4 (C_1 of β anomer), 87.0 and 85.2 (C_2), 83.3 and 83.0 (C_4), 81.3 and 76.3 (C_3), 79.9 and 77.6 (C_5), 72.2 and 72.0 (C_6), 60.7—55.2 (OMe).

Methyl D-Glucofuranoside Tetramethyl Ether 24. To a solution of 1,2-*O*-isopropylidene-D-glucofuranose (250 mg, 1.14 mmol) in dry THF (20 ml) was added NaH (400 mg, 16.7 mmol), and the mixture was stirred for 30 min. Methyl iodide (1.6 ml, 25 mmol) was added and the mixture was stirred for 18 h at room temperature. Methanol was added to quench the excess NaH, and the solution was concentrated in vacuo. Water was added, and the products were extracted with $CHCl_3$. After dried over Na_2SO_4, the solvent was removed in vacuo to give an oil. The oil (302 mg) was dissolved in methanol (12 ml) and 98% H_2SO_4 was added slowly. The solution was stirred for 20 h at room temperature, poured into water, and extracted with ether. After the extract was dried over Na_2SO_4, the solvent was removed in vacuo to give an oil, 220 mg. The oil was again methylated in the same way as above, and the crude product was distilled to afford a pure sample of **24**, 220 mg, bp 110 °C (0.03 mmHg). For **24**: GC-MS, *m/z* (rel intensity) 205 (M^+—CH_2OMe, 0.8), 173 (2.0), 161 (7.5), 145 (5.8), 101 (100), 75 (65.0), 59 (16.8), 45 (61.3). ^{1}H NMR ($CDCl_3$), δ=3.26—3.48 (15H, singlets, OMe), 3.47—3.91 (5H, m, H_2-H_6), 3.95—4.23 (1H, m, H_4), 4.81 (1/2H, s, H_1 of β anomer (1R)), 4.92 (1/2H, d, J=3.0 Hz, H_1 of α anomer (1S)). ^{13}C NMR ($CDCl_3$), δ=108.1 (C_1 of β anomer), 101.1 (C_1 of α anomer), 87.4 and 86.1 (C_2), 83.8 and 82.7 (C_4), 79.7 and 76.3 (C_3), 78.0 and 77.7 (C_5), 72.6 and 72.4 (C_6), 59.2—55.1 (OMe).

Trimethylsilyl Triflate-Catalyzed Allylation of 4c and 4d To a solution of **4c** (80 mg, 0.33 mmol) in dry acetonitrile (3 ml) was added allyltrimethylsilane (1.6 ml, 1 mmol), and then TMSOTf (0.01 ml, 0.05 mmol) at −30 °C. The mixture was stirred at this temperature for 20 min, and the workup in the same way as for **4b** gave a product **13c** (83 mg, 98% yield). The pure sample was obtained by a preparative TLC. In the same way, benzyl derivative **13d** was obtained from **4d** in 60% yield. For **13c** (as an anomeric mixture): GC-MS, *m/z* (rel intensity) 215 (M^+—OMe, 0.08), 205 (3.5), 173 (3.5), 161 (6.7), 145 (4.3), 101 (99.9), 85 (32.0), 75 (100). ^{1}H NMR (CCl_4), δ=2.09—2.33 (2H, m, -$C\underline{H}_2$-$CH=CH_2$), 3.28—3.45 (12H, singlets, OMe), 3.09—4.03 (4H, m, H_2-H_5), 4.65—5.16 (3H, m, H_1, $C\underline{H}_2$=CH-), 5.28—6.11 (1H, m, CH_2=C$\underline{H}$-). For **13d** (as an anomeric mixture): ^{1}H NMR (CCl_4), δ=2.07—2.56 (2H, m, $C\underline{H}_2$-$CH=CH_2$), 3.20—3.35 (6H, singlets, OMe), 3.62—4.09 (4H, m, H_2-H_5), 4.43 (4H, s, benzyl-CH_2), 4.72—5.11 (3H, m, H_1, $C\underline{H}_2$=CH-), 5.42—6.25 (1H, m, CH_2=C$\underline{H}$-), 7.25 (10H, s, Ar).

Butylation of 4d. To a solution of **4d** (130 mg, 0.33 mmol) in CH_2Cl_2 (3 ml) was added $TiCl_4$ (0.04 ml, 0.33 mmol) at −78 °C. A hexane solution of 1.4 M *n*-BuLi (0.72 ml, 1 mmol) was added at this temperature, and the mixture was warmed up to room temperature. After stirring for 1 h at room temperature, the mixture was worked up in conventional way to produce **15d** (132 mg, 64% yield) as an oil. Preparative TLC gave a pure sample. For **15d**: ^{1}H NMR (CCl_4), δ=[0.95 (3H, m) and 1.30 (6H, m), *n*-Bu], 3.21—3.37 (6H, singlets, OMe), 3.40—3.61 (1H, m, H_5), 3.73—4.22 (3H, m, H_2, H_3, H_4), 4.40—4.48 (4H, singlets, benzyl-CH_2), 4.55—4.80 (1H, m, H_1), 7.20 (10H, s, Ar).

Wacker Oxidation of 13b to 14b. Oxygen gas was bubbled into a solution of $PdCl_2$ (6.7 mg, 0.038 mmol) and CuCl (40 mg, 0.40 mmol) in a mixture solvent of DMF (1 ml) and water (0.4 ml) for 30 min. To the solution was added **20b** (103 mg, 0.34 mmol), and oxygen gas was bubbled into the solution for another 6 h. After 3 M HClaq (0.2 ml) was added, the solution was shaken with CH_2Cl_2. The extract was washed with Na_2CO_3aq and then with NaClaq. After dried over Na_2SO_4, the solvent was removed in vacuo. The crude material (120 mg) was purified on a preparative TLC to give an oil which was identical with **14b** obtained from **4b**.

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6) Due to the uncertainty concerning with the newly-created asymmetric center at C5, the anomeric nomenclature of α and β is ambiguous. Throughout the present paper, therefore, we termed α for all compounds having the same anomeric configuration as that of α-D-glucose.

7) The assumption could be generally supported because, with some compounds in which the α and β anomeric protons resonate at separate positions, the estimation from ^{13}C NMR and ^{1}H NMR spectra coincided.

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