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Metal-Catalyzed Organic Photoreactions. Iron(III)-Catalyzed Photoreactions of Aldo- and Ketohexoses[1)]

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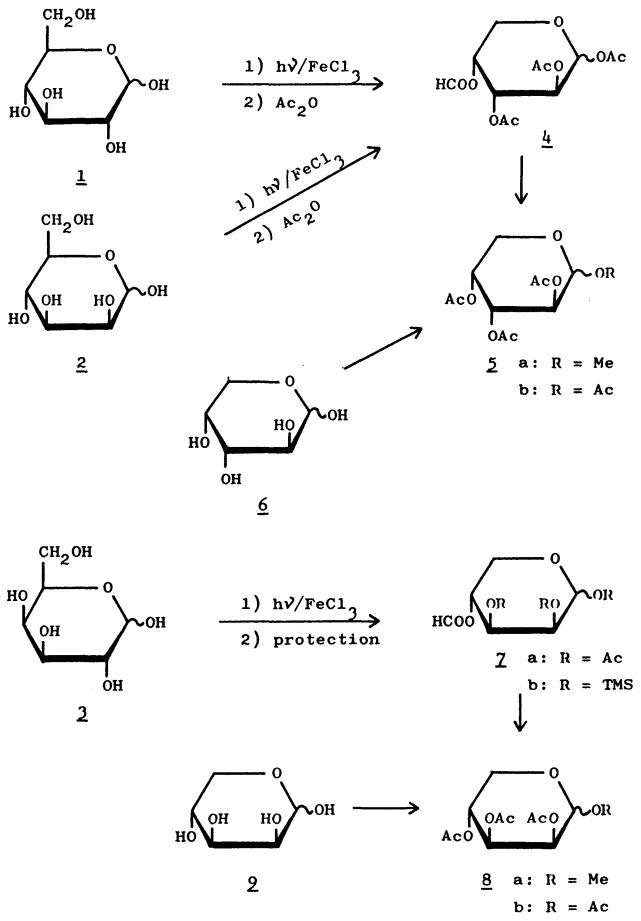
Under UV irradiation in the presence of iron(III) chloride or iron(III) triflate in pyridine, D-glucose, D-mannose, and D-galactose underwent a selective bond cleavage at the C1-C2 position, producing 4-*O*-formyl-D-arabinopyranose and 4-*O*-formyl-D-lyxopyranose. D-Fructose, under the same conditions, gave arabino-γ-lactone. The reaction was interpreted in terms of the photoinduced electron transfer within a chelate of iron ion with the carbohydrate molecule.

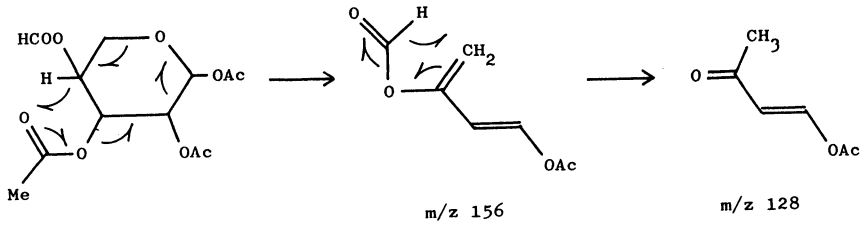
In our preceding papers,[2)] we found that the UV irradiation of D-glucose, D-mannose, and D-galactose in methanol in the presence of titanium(IV) chloride induced a selective bond cleaveage of C5-C6 bond of the carbohydrates, producing corresponding pentodialdose derivatives. It was also found that the aldehyde functions in these dialdose derivatives reacted with several nucleophiles with relatively high chemo- and stereoselectivities. In view of our previous observations[3)] that iron(III) chloride, as well as titanium(IV) chloride, exhibited remarkable effects upon the photoreaction of organic molecules, and that the iron(III) chloride-catalyzed photoreaction proceeded most satisfactorily in pyridine, we irradiated several monosaccharides under these reaction conditions, and found now that the iron(III)-catalyzed photoreaction of the carbohydrates in pyridine induced a selective cleavage of C1-C2 bond, in contrast to the C5-C6 bond cleavage by titanium(IV) chloride, and afforded pentose derivatives having formate function only at the C4 position. In view of good selectivity of the reaction and possible utility of the products as chiral synthons, we investigated the reaction in detail.

A pyridine solution of D-glucose (**1**) containing an equivalent amount of iron(III) chloride was irradiated with a high-pressure mercury lamp in a Pyrex tube for 24 h while oxygen gas was bubbled through. After irradiation, the products were isolated as acetates by treating the irradiated solution with acetic anhydride. The major product was an anomeric mixture of an aldopentose derivative **4** (α/β=1/1) in 38% yield, along with the starting material as pentaacetate in 41% yield (Scheme 1). D-Mannose (**2**) gave the same product **4** in 17% yield under the same conditions, along with the starting material as pentaacetate in 74% yield.

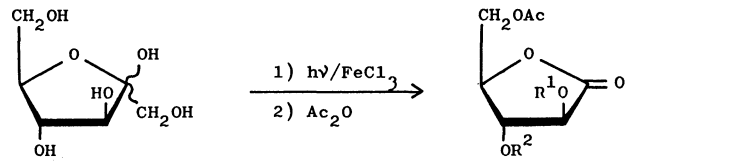
The structure **4** was determined in the following way. When the product **4** was treated first with titanium(IV) chloride in methanol, and then with acetic anhydride in pyridine, an oil was obtained which showed two peaks on a gas chromatogram. The oil proved to be an anomeric mixture of methyl D-arabinopyranoside triacetate (**5a**), because the same mixture was obtained by treating D-arabinose (**6**) with titanium(IV) chloride in methanol, followed by acetylation under the same conditions as above. The pyranose ring form for **4** was deduced from the fragmentation pattern of the mass spectrum, in which the M^+-73 peak, typical for the furanose structure (loss of the side chain),[4)] was lacking. The ^{1}H NMR spectrum of **4** indicated the presence of C5 methylene, referring to the data reported for **5b**.[5)] The position of the formate was assigned at C4 in view of the fragmentation peaks at *m/z* 156 and 128 of the mass spectrum, which could be ascribed to the ions depicted in Scheme 2, referring to the general mass spectrum fragmentation pattern of acylated pyranoses proposed by Biemann and his group.[6)]



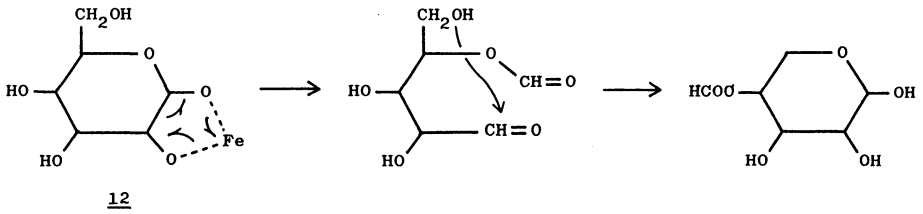
Scheme 1.



Scheme 2.



Scheme 3.



Scheme 4.

D-Galactose (**3**) gave an anomeric mixture **7a** (α/β=7/3) in 35% yield under the same conditions, with the recovery of the starting material in 36% yield. The structure **7a** was confirmed by converting the product into an anomeric mixture of D-lyxoside derivatives **8a**, which was identicai with that obtained from D-lyxose (**9**) in the same way as described for arabinose. When the irradiated solution was treated with trimethylsilyl chloride, a silyl derivative **7b** was isolated. By referring to the ^{13}C NMR spectrum, the product proved to be a single diastereomer. In contrast to the acetate **7a**, the NMR signal of proton on the formate-carrying carbon in **7b** appeared at well separated position from those of the other ring protons, featuring a definite ABMX fine structure. The similar pattern was also observed in **18b** and **18c**. This would be an another indication that the formate function stays at C4 position.

When D-fructose (**10**), a ketohexose, was irradiated under the same conditions, **11a** was obtained in 52% yield after the acetylation (Scheme 3). Evidently the reaction proceeded with selective bond cleavage at C1-C2 position as in the case of aldohexoses. The photoreaction of the ketose was faster than that of the aldohexoses, and no starting material was recovered after the irradiation for 5 h. The structure **11a** was confirmed by comparing the spectroscopic data with those of γ-D-ribonolactone triacetate, synthesized by the reported method.[7]

It has been known that D-glucose does produce D-arabinose under the irradiation in the presence of molecular oxygen in aqueous solution, and the reaction has been believed to be initiated by hydroxyl radical, giving many compounds in small quantities.[8] In view of the facts that the iron(III) chloride-catalyzed photolysis proceeded quite selectively, producing D-arabinose as the main product, and that the reaction proceeded even in the absence of molecular oxygen and water, the possibility of a mechanism involving any species originated from molecular oxygen or water was ruled out. We propose a reaction involving an electron transfer within an iron chelate **12**, followed by the recyclization of the fission product as shown in Scheme 4. In support of this scheme, methyl D-glucopyranoside and 1,2-*O*-isopropylidene-α-D-glucofuranose, lacking the system for the chelate formation, did not undergo the present reaction, and the starting materials were recovered as acetates.

The present reaction proceeded even in the absence of molecular oxygen, although the reaction was much slower under these conditions. Referring to the reaction scheme, iron(III) should have been reduced to iron(II). Presumably, molecular oxygen reoxidized the iron(II) to iron(III), thus resulting in the enhancement of the reaction efficiency. Expectedly, iron(III) chloride behaved as a catalyst in the presence of molecular oxygen, and the reaction proceeded effectively even with 1/100 equivalent of iron(III) to the carbohydrate

molecules, although the amounts of by-products increased to some extent under these conditions.

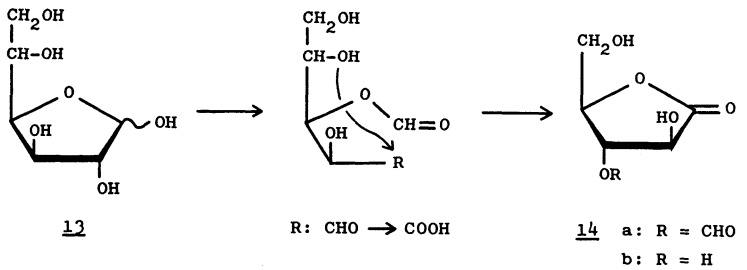
Although the yields of the present reaction were not necessarily high, the reaction was quite selective and the amounts of the smaller fragments or the products resulted from the bond cleavage at other positions were small. Remarkably, the reaction proceeded only in pyridine in the presence of iron(III) ion. The reaction using other metal salts or solvents gave poor results with little or no amounts of the aldopentoses. Later, we found that iron(III) trifluoromethanesulfonate (triflate) gave even better results than iron(III) chloride. Iron(III) triflate catalyzed the reaction more effectively than the chloride, and hence we could reduce the irradiation time and the amount of the metal compound extensively as shown in Table 1. Even in case of using only 1/100 equivalent of iron(III) triflate, the reaction proceeded quite cleanly, in contrast to the corresponding case using iron(III) chloride.

It has been known that the thermal oxidation of aldohexoses by lead(IV) acetate involves the initial cleavage of C1-C2 bond, followed by a stepwise shortening of the carbon chain.[9] As a comparison with these observations, we examined the thermal reaction of D-glucose and D-fructose under the otherwise same conditions as those of the present photoreaction. As in the case of the photoreaction, the thermal reaction of the ketose was faster than that of the aldose. Upon heating in pyridine at 100 °C in the presence of iron(III) chloride, D-glucose (**1**) gave two compounds **11a** and **11b** as the exclusive product after the acetylation. The triacetate **11a** was the exclusive product of the thermal reaction of D-fructose (**10**), indicating that the reaction pattern of the ketose was the same in the photo and thermal reactions. However, no trace of the photoproduct **4** was identified in the thermal reaction of D-glucose. The structure **11b** was deduced in view of the NMR and mass spectra, which showed that both **11a** and **11b** have identical gross structure. Although we could not distinguish experimentally between two possible structures of 2- and 3-formate for **11b**, the 3-formate structure would be preferable in view of the following reaction scheme (Scheme 5). It has been known that the lead(IV) acetate oxidation of D-glucose proceeds faster from furanose form than from pyranose form.[10] It could be assumed that the iron(III) chloride-initiated oxidation also proceeded from the furanose form of D-glucose **13**, and probably due to the overoxidation of the aldehyde intermediate, the product would be a lactone **14a**. The product suffered a partial hydrolysis of the formate group under the reaction conditions to give **14b**, and afforded the observed products **11a** and **11b** upon acetylation after the reaction. Remarkably, these observations show that the photoreaction proceeds from the pyranose structure, while the thermal reaction proceeds from the furanose structure, both structures being in an equilibrium under the present reaction conditions.

Table 1. Catalytic Activities of Iron(III) Chloride and Iron(III) Triflate in the Photoreaction of **1**

Iron salt	Mol ratio to carbohydrate	Reaction time / h	Relative yield/%	
			Product	Starting material
$FeCl_3$	1	24	45	55
$Fe(OTf)_3$	1	24	64	36
$FeCl_3$	1	2	15	85
$Fe(OTf)_3$	1	2	39	61
$FeCl_3$	1/100	24	19	81
$Fe(OTf)_3$	1/100	24	44	56
$FeCl_3$	1/100	2	7	93
$Fe(OTf)_3$	1/100	2	29	71

Shiraishi and his group reported that the photooxidation of D-glucose and D-mannose in the presence of iron(III) chloride in aqueous solution produced D-erythrose (**15a**) as major product, accompanied in some cases by a minor amount of D-arabinos (**6**).[11] They also found that D-erythrose was the sole product from D-fructose under their conditions. In search for the tetrose derivatives in our reaction, we carefully checked the foreruns obtained in small amounts, and isolated **15b** from **1** and **2** in 3% and 0.7% yields, respectively, and D-threose derivative **16** from **3** in 2.5% yield. We assumed that these compounds were produced by the C1-C2 bond cleavage of the primary products corresponding to **4** and **7**, followed by the ring closure in the similar way as that shown in Scheme 4. When D-arabinose (**6**) was irradiated under the same conditions, **15b** was obtained in 4% yield, while the starting material **6** was recovered as tetraacetate in 63% yield. D-Xylose, an another pentose, was also decomposed only to a minor extent under the same conditions, with the recovery of the starting material in 60% yield.



Scheme 5.

These observations indicate that the reaction from the aldopentoses is much slower than that from the aldohexoses. Although we can offer no reasonable explanation for the difference in the reactivity, it should be this difference that makes the present photoreaction fairly selective, terminating the photocleavage at the stage of pentose.

The UV spectroscopic studies also showed that an iron chelate system played an important role in our reaction. We observed that the intensity of the peak at 346 nm in the UV spectrum of iron(III) chloride in pyridine was decreased by the addition of the carbohydrate molecules. Figure 1 shows the change of the UV spectrum of iron(III) chloride in pyridine upon addition of D-galactose up to 100 equivalents. The same trend was observed with other carbohydrates, but the extent of the effect differed from one carbohydrate to another. In Fig. 2 are shown the spectra of iron(III) chloride in pyridine with several carbohydrates added in 100-fold excess. The absorption at 346 nm has been ascribed to the charge transfer from chloride ligand to iron(III) ion.[12] In accord with the assignment, iron(III) triflate did not show any peak in this region, as shown in Fig. 1. We speculated that the addition of the carbohydrate molecules resulted in the expulsion of the chloride ligand from the iron coordination sphere due to the iron chelate formation with the carbohydrate molecule, and we believed that this would be an experimental evidence for the reaction scheme proposed as shown in Scheme 4. myo-Inositol, a carbocyclic polyhydroxy compound, did not undergo the present type of the C-C bond cleavage. Notably, the UV spectrum of iron(III) chloride in pyridine was not affected at all by the addition of myo-inositol or ethylene glycol as the typical 1,2-diol system. Presumably, the presence of 1,2-diol system involving anomeric hydroxyl group was responsible for the chelate formation, and the chelate formation might be requisite for the present reaction to proceed. Although D-fructose, which exhibited the largest effect, actually underwent

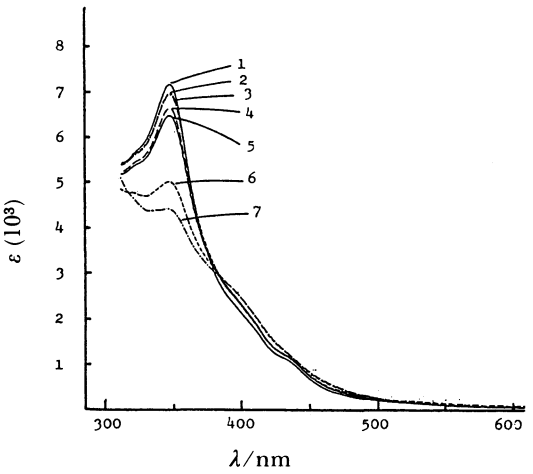


Fig. 1. Change of UV spectrum of iron(III) chloride in pyridine as a function of concentration of D-galactose. $FeCl_3$: 2.25×10^{-4} M. D-Galactose: $n\times 2.25\times10^{-4}$ M; 1: n=0; 2: n=1; 3: n=5; 4: n=10; 5: n=20; 6: n=60; 7: n=100.

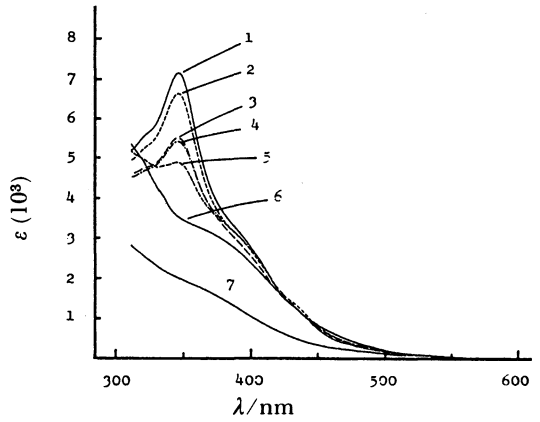
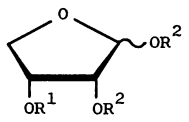
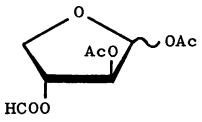


Fig. 2. Change of UV spectrum of iron(III) chloride in pyridine upon addition of carbohydrates (1—6), and UV spectrum of iron(III) triflate in pyridine (7). $FeCl_3$: 2.44×10^{-4} M, $Fe(OTf)_3$: 2.31×10^{-4} M. Carbohydrates: 2.27×10^{-2} M; 1: none; 2: D-glucose; 3: D-galactose; 4: D-mannose; 5: D-fructose; 6: D-arabinose; 7: none.



15 a: $R^1 = R^2 = H$
b: R^1 = CHO
R^2 = Ac



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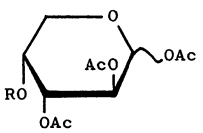
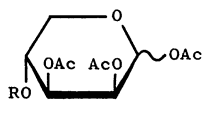
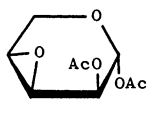


17 a: R = H
b: R = p-tolSO$_2$



18 a: R = H
b: R = p-tolSO$_2$
c: R = MeSO$_2$



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the photoreaction most efficiently, there seemed to be no direct correlation between the reactivity and the extent of the influence upon UV spectrum.

The most characteristic point of the present reaction is that the aldohexoses produce the aldopentoses in which only C4 hydroxyl group is protected by formyl group. With a hope to utilize the products as chiral synthons for the synthetic chemistry, the selective manipulation of the formate group was next explored.

When the acetate **4** or **7a** was treated with aluminum chloride in an aqueous methanol, formyl group was removed selectively, producing anomeric mixture of **17a** or **18a** in 84% or 94% yield, respectively. The acetylation of **17a** afforded the corresponding anomeric mixture of tetraacetates **5b**, identical with the authentic samples prepared by the known method.[13] The column chromatography of **7a** afforded pure α anomer, which, upon the selective hydrolysis of the formate and succeeding acetylation, gave pure α anomer of **8b**, identical with the authentic sample.[14] This would be a reasonable indication that no neighboring group participation inducing the possible scrambling of the stereochemistry was involved under these conditions. Tosylation or mesylation of **17a** or **18a** gave the corresponding derivatives **17b**, **18b**, or **18c**. The tosylate **18b**, upon treatment with sodium methoxide, produced L-ribose derivative **19** in 53% yield. We are exploring further applicability of the photoproducts for the synthesis of chiral compounds.

Experimental

The general procedures and instrumentation were the same as those reported in our preceding paper.[2] The NMR spectral assiments were based on the data of structurally similar system.[5,15,16]

Iron(III) Chloride-Catalyzed Photoreaction of D-Glucose (1). A pyridine solution (150 ml) of D-glucose (**1**, 1.50 g, 8.3 mmol) and $FeCl_3 \cdot 6H_2O$ (2.25 g, 8.3 mmol) was irradiated in a Pyrex tube for 24 h while oxygen gas was bubbled through. Acetic anhydride (15 ml, 166 mmol) was added to the solution, and the solution was stirred for 12 h at room temperature. The solution was concentrated in vacuo, washed with dil HClaq, extracted with dichloromethane, and dried over $MgSO_4$. The distillation gave two main fractions. The main product **4** was obtained as the lower boiling fraction, bp 148—150 °C (0.35 mmHg (1 mmHg=133.322 Pa)), 0.958 g, 38% yield, and showed two peaks (1 : 1) on a gas chromatogram which were assigned as α and β anomers, referring to the spectroscopic data and chemical reactions described below. Since the separation of both anomers were unsuccessful, the spectroscopic data were obtained on the mixture sample. For **4**: GC-MS, m/z (for α anomer) 245 ($M^+ - OAc$, 10.7), 170 (20.2), 156 (60.0), 145 (65.8), 128 (73.1), 103 (78.4), 97 (100): (for β anomer) 245 ($M^+ - OAc$, 10.4), 170 (20.9), 156 (74.1), 145 (77.4), 128 (93.4), 103 (100), 97 (92.1). ^1H NMR ($CDCl_3$) δ=2.01—2.17 (9H, s, Ac), 3.75—4.34 (2H, m, H_5, $H_{5'}$), 5.11—5.53 (3H, m, H_2, H_3, H_4), 5.68 (1/2H, d, J=6.2 Hz, α-H_1), 6.32 (1/2H, d, J=3.7 Hz, β-H_1), 8.14 and 8.17 (1H, s×2, CHO).[5] ^{13}C NMR ($CDCl_3$) δ=20.5 and 20.7 (Ac-Me), 62.4 and 63.6 (C_5), 66.5 and 66.9 (C_4), 68.0 and 68.1 (C_2), 69.7 and 69.8 (C_3), 90.0 and 92.0 (C_1), 159.6—159.8 (CHO), 168.8—170.3 (Ac-CO).[15] HRMS, Found: m/z 245.0686. Calcd for $C_{10}H_{13}O_7$ ($M-OAc$): 245.0661.

The higher boiling fraction, bp 160 °C (0.35 mmHg), crystallized upon standing, mp 109—115 °C, 1.33g. The compound was identical (GLC, NMR, and MS) with the sample of D-glucose pentaacetate,[17] prepared by the reported method.

The minor amount of the forerun (bp 134—138 °C (0.15 mmHg)) was mostly **15b** (3% yield), identical with the sample obtained by the photoreaction of D-arabinose (see below).

Methyl D-Arabinoside Triacetate (5a). A mixture of **4** (50 mg, 0.16 mmol) and $TiCl_4$ (0.5 ml, 4.6 mmol) in dry methanol (10 ml) was refluxed for 12 h, and the solution was neutralized with dil NaOHaq. The precipitate was removed by the filtration and the filtrate was concentrated to dryness in vacuo. The residue was distilled with a Kugelrohr, bp 100 °C (0.05 mmHg), 38 mg, 80% yield, to afford **5a**. This was completely identical (GLC, NMR, MS) with the sample prepared from D-arabinose under the same conditions. For **5a**: GC-MS, m/z (rel intensity) 259 ($M^+ - OMe$, 2.2), 199 (1.6), 170 (56.5), 128 (73.8), 69 (100). ^1H NMR ($CDCl_3$) δ=2.02—2.14 (9H, s, Ac), 3.41 (3H, s, OMe), 3.63—4.03 (2H, m, H_5, $H_{5'}$), 4.34 (3/5H, m, H_1 of α anomer), 4.91 (2/5H, d, J=3.2 Hz, H_1 of β anomer), 5.07—5.27 (3H, m, H_2, H_3, H_4).

Iron(III) Chloride-Catalyzed Photoreaction of D-Glucose (1) under Anhydrous and Anaerobic Conditions. The reaction solution was prepared from anhydrous reagents and solvent, applying freezing and thawing method. The yield of the product **4** was 13%, and the starting material was recovered in 75% as pentaacetate.

Iron(III) Chloride-Catalyzed Photoreaction of D-Mannose (2). The reaction and the subsequent acetylation were carried out in the same way as described for D-glucose. The product **4**, bp 145—150 °C (0.3 mmHg), was identical with that obtained from D-glucose. The higher boiling fraction, bp 160 °C (0.3 mmHg), was D-mannose pentaacetate, identical with the product prepared from D-mannose. As in the case of D-glucose, **15b** (0.7% yield) was also isolated from the small amount of the forerun, bp 110 °C (0.05 mmHg).

Iron(III) Chloride-Catalyzed Photoreaction of D-Galactose (3). The reaction and the subsequent acetylation were carried out in the same way as described for D-glucose. The crude product gave two fractions as main portion upon distillation. The lower boiling fraction **7a**, bp 156—158 °C (0.2 mmHg), showed two peaks on a gas chromatogram with relative ratio of 7 : 3. The mass spectrum of each component was quite similar to that of **4**. The column chromatography of the crude product gave the major component α-**7a** in pure state, while β-**7b** was not freed from the α anomer. For α-**7a**: GC-MS, m/z (rel intensity) 245 ($M^+ - OAc$, 3.5), 156 (48.9), 145 (57.5), 114 (47.4), 103 (91.1), 97 (100), 69 (68.4). ^1H NMR ($CDCl_3$) δ=2.05, 2.16, and 2.17 (9H, 3s, Ac), 3.73—4.28 (2H, m, H_5, $H_{5'}$), 5.21—5.42 (3H, m, H_2, H_3, H_4), 6.05 (1H, d, J=3.1 Hz, H_1), 8.08 (1H, s, CHO). ^{13}C NMR ($CDCl_3$) δ=20.6 and 20.8 (Ac-Me), 61.6 (C_5), 66.1 (C_2), 68.1 (C_4), 68.2 (C_3), 90.6 (C_1), 159.4 (CHO), 168.3, 169.4 and 169.6 (Ac-CO). HRMS, Found: m/z 245.0690. Calcd for $C_{10}H_{13}O_7$ ($M-OAc$): 245.0661. For β-**7a**: GC-MS, m/z (rel intensity) 245 ($M^+ - OAc$, 4.0), 170 (10.4), 156 (44.6), 145 (51.4), 128 (56.9), 114 (63.3), 103 (85.4), 97 (100), 73 (89.5), 69 (93.5). ^{13}C NMR

($CDCl_3$, obtained by subtracting the data of α anomer from those of the mixture) δ=20.6 and 20.8 (Ac-Me), 61.2 (C_5), 66.4 (C_2), 67.1 (C_3), 67.8 (C_4), 89.7 (C_1), 159.4 (CHO), 168.2—170.7 (Ac-CO).

The forerun (bp 135—140 °C (0.2 mmHg)), obtained in only small amount, was mostly **16** (2.5% yield). The pure sample was obtained by a preparative GLC. For **16**: GC-MS, m/z (rel intensity) 173 (M^+ −OAc, 14.4), 127 (9.2), 101 (32.3), 85 (100), 73 (61.9). ^{1}H NMR ($CDCl_3$) δ=2.07—2.21 (6H, s, Ac), 3.81—4.75 (2H, m, H_4, $H_{4'}$), 5.25—5.60 (2H, m, H_2, H_3), [6.16 (1/2H, s) and 6.45 (1/2H, d, J=4.8 Hz), H_1], 8.15 (1H, s, CHO).

When the irradiated solution from 200 mg of D-galactose was refluxed for 1 h with chlorotrimethylsilane (5 ml) and hexamethyldisilazane (6 ml) being added, an oil (484 mg) was obtained after the purification on a Florisil column. The oil was further separated into two fractions of R_f's 0.7 and 0.6 on a preparative TLC ($CHCl_3$). The former fraction was identical (NMR, GC-MS) with the authentic pentakis-*O*-trimetylsilyl-D-galactose (298 mg, 50% yield). The latter fraction was **7b**, 151 mg, 34% yield. For **7b**: GC-MS, m/z (rel intensity) 394 (M^+, 0.26), 305 (2.4), 231 (11.1), 217 (32.9), 204 (100), 191 (89.1). ^{1}H NMR ($CDCl_3$) δ=0.14—0.17 (27H, s, TMS), 3.61 (1H, dd, $J_{2,1}$=4.6 and $J_{2,3}$=3.1 Hz, H_2), 3.65 (1H, dd, $J_{5',4}$=6.3 and $J_{5',5}$=12.0 Hz, $H_{5'}$), 3.85 (1H, dd, $J_{5,4}$=3.5 and $J_{5,5'}$=12.0 Hz, H_5), 3.98 (1H, dd, $J_{3,2}$=3.1 and $J_{3,4}$=6.4 Hz, H_3), 4.86 (1H, d, $J_{1,2}$=4.6 Hz, H_1), 4.95 (1H, ddd, $J_{4,3}$=6.4, $J_{4,5'}$=6.3, $J_{4,5}$=3.5 Hz, H_4). ^{13}C NMR ($CDCl_3$) δ=0.1, 0.5, and 0.6 (TMS), 61.4 (C_5), 70.5 (C_4), 71.5 (C_2), 73.4 (C_3), 95.4 (C_1), 160.1 (CHO). HRMS, Found: m/z 394.1573. Calcd for $C_{15}H_{34}O_6Si_3$ (M): 394.1618.

Methyl D-Lyxoside Triacetate (8a). A mixture of **7a** (51 mg, 0.17 mmol) and 12 M HCl (0.1 ml) (1M=1 mol dm^{-3}) in methanol (8 ml) was refluxed for 12 h. The solution was neutralized with dil NaOH and concentrated in vacuo. To the residue was added dry pyridine (5 ml) and acetic anhydride (2 ml), and the mixture was kept at room temperature for 7 h. Pyridine and acetic anhydride were removed in vacuo, and the residue was passed through a column (silica gel/$CHCl_3$) to produce **8a**, 37 mg, 77% yield, identical with the sample prepared from D-lyxose under the same conditions. For **8a**: GC-MS, m/z (rel intensity) 259 (M^+ −Me, 2.0), 199 (2.2), 170 (40.7), 128 (100), 115 (38.5). ^{1}H NMR ($CDCl_3$) δ=2.01—2.12 (9H, s, Ac), 3.38 (1H, s, OMe), 3.58—4.09 (2H, m, H_5, $H_{5'}$), 4.69 (1H, d, J=2.2 Hz, H_1), 4.97—5.29 (3H, m, H_2, H_3, H_4).

Iron(III) Triflate-Catalyzed Photoreaction of D-Glucose (1) and D-Galactose (3). Iron(III) triflate was prepared in the following way. Trifluoromethanesulfonic acid (12.3 g, 81.6 mmol) was gradually added to crystals of $Fe(NO_3)_3 \cdot 9H_2O$ (10.0 g, 24.8 mmol), and the mixture was heated to 250 °C in a porcelain vessel placed on a sand bath until the evolution of nitrogen oxides and water was not noticed. The white crystalline material (12.3 g, 99% yield) was allowed to cool in a desiccator, and used without further purification.

The photolyses of D-glucose (5.56 mmol) and D-galactose (5.56 mmol) were carried out using $Fe(OTf)_3$ (0.056 mmol), under the otherwise same conditions described for the $FeCl_3$-catalyzed photoreactions. The products **4** and **7a** were obtained in 32—40% yield and 29—36% yields, respectively.

1,2,3-Tri-*O*-acetyl-D-lyxopyranose (18a) and 1,2,3,-Tri-*O*-acetyl-D-arabinopyranose (17a). To a solution of **7a** (273 mg, 0.9 mmol, α/β=7/3) in a mixture solvent of methanol (20 ml) and water (1 ml) was added $AlCl_3$ (12 mg, 0.09 mmol) gradually, and the solution was stirred for 13 h at room temperature. The solution was concentrated in vacuo, and water (15 ml) was added. The mixture was shaken with dichloromethane, and, after the extract was dried over $MgSO_4$, the solvent was removed in vacuo. When the remaining oil was passed through a short column of Florisil, **18a** (273 mg, 94% yield) was obtained. Referring to the NMR signals of anomeric protons, the product was a mixture of α and β anomers with a ratio of 7 : 3. Purification on a preparative TLC (silica gel/$CHCl_3$–AcOEt (1 : 1)) gave a pure sample of major component, α-**18a**, 152 mg, 61% yield. For α-**18a**: ^{1}H NMR ($CDCl_3$) δ=2.08, 2.12 and 2.15 (9H, s×3, Ac), 2.96 (1H, br d, OH), 3.54—4.26 (3H, m, H_4, H_5, $H_{5'}$), 5.16 (1H, dd, $J_{3,2}$=3,3 and $J_{3,4}$=9.1 Hz, H_3), 5.22 (1H, dd, $J_{2,1}$=2.6 and $J_{2,3}$=3.3 Hz, H_2), 5.96 (1H, d, $J_{1,2}$=2.6 Hz, H_1). ^{13}C NMR ($CDCl_3$) δ=20.6 and 20.8 (Ac-Me), 64.6 (C_5), 65.0 (C_4), 68.4 (C_3), 71.6 (C_2), 90.9 (C_1), 168.5, 169.5 and 179.5 (Ac-CO). HRMS, Found: m/z 276.0845. Calcd for $C_{11}H_{16}O_8$ (M): 276.0891.

The hydrolysis of **4** (1.0 g) was carried out under the same conditions as above to afford the product **17a** (0.763 g, 84% yield). The column chromatography (silica gel/$CHCl_3$) gave β-**17a** in pure state, while α-**17a** was not completely freed from β-**17a**. For β-**17a**: ^{1}H NMR ($CDCl_3$) δ=2.08, 2.12 and 2.15 (9H, s×3, Ac), 2.98 (1H, br s, OH), 3.83 (1H, dd, $J_{5',4}$=2.2 and $J_{5',5}$=12.8 Hz, $H_{5'}$), 4.05 (1H dd, $J_{5,4}$=1.1 and $J_{5,5'}$=12.8 Hz, H5), 4.19 (1H, br, H_4), 5.25 (1H, dd, $J_{2,1}$=3.3 and $J_{2,3}$=9.4 Hz, H_2), 5.45 (1H, dd, $J_{3,2}$=9.4 and $J_{3,4}$=3.0 Hz, H_3), 6.31 (1H, d, $J_{1,2}$=3.3 Hz, H_1). ^{13}C NMR ($CDCl_3$) δ=20.55, 20.64 and 20.8 (Ac-Me), 64.6 (C_5), 66.7 (C_4), 67.3 (C_2), 69.6 (C_3), 90.4 (C_1), 169.1, 169.9 and 170.1 (Ac-CO). For α-**17a** (obtained by subtracting the data of β anomer from those of the mixture): ^{1}H NMR ($CDCl_3$) δ=2.06—2.15 (9H, s, Ac), 3.19 (1H, br, OH), 3.65—4.18 (3H, m, H_4, H_5, $H_{5'}$), 5.12—5.58 (2H, m, H_2, H_3), 5.67 (1H, d, J=6.2 Hz, H_1). ^{13}C NMR ($CDCl_3$) 20.62, 20.67 and 20.8 (Ac-Me), 65.2 (C_5), 65.6 (C_4), 68.3 (C_2), 72.0 (C_3), 91.8 (C_1), 169.0, 169.3 and 170.1 (Ac-CO).

1,2,3-Tri-*O*-acetyl-4-*O*-methylsulfonyl-D-lyxopyranose (18c). To a solution of **18a** (373 mg, 1.35 mmol, α/β=75/25) in dry pyridine (15 ml) was added methanesulfonyl chloride (0.4 ml, 5.2 mmol) dropwise with stirring. The reaction mixture was kept overnight at room temperature, and the solvent was removed in vacuo. The excess of the reagent was decomposed by the cautious addition of cooled water (15 ml), and the product was extracted with dichloromethane. After washed with water and dried over $MgSO_4$, the extract was passed through a Florisil column to give white crystals as an anomeric mixture of **18c**, mp 142—147 °C, 391 mg, 82% yield, α/β=8/2. Column chromatography (silica gel/ether) gave a pure sample of α-**18c**, 301 mg, 63% yield. For α-**18c**; mp 145—146 °C. GC-MS, m/z (rel intensity) 354 (M^+, 1.1), 295 (5.9), 206 (61.1), 193 (26.2), 181 (55.0), 139 (79.5), 114 (69.1), 68 (100). ^{1}H NMR ($CDCl_3$) δ=2.07 and 2.16 (9H, s×2, Ac), 3.06 (3H, s, $MeSO_2$), 3.74 (1H, dd, $J_{5',4}$=9.1 and $J_{5',5}$=11.1 Hz, $H_{5'}$), 4.13 (1H, dd, $J_{5',4}$=5.5 and $J_{5,5'}$=11.1 Hz, H_5), 4.98 (1H, ddd, $J_{4',3}$=9.2, $J_{4,5}$=5.5 and $J_{4,5'}$=9.1 Hz, H_4), 5.29 (1H, dd, $J_{2,1}$=2.2 Hz and $J_{2,3}$=3.2 Hz, H_2), 5.40 (1H, dd, $J_{3,2}$=3.2 and $J_{3,4}$=9.4 Hz, H_3), 6.01 (1H, d, $J_{1,2}$=2.2 Hz, H_1). ^{13}C NMR ($CDCl_3$) δ=19.8, 19.9 and 21.2 (Ac-Me), 38.2 ($MeSO_2$), 62.0 (C_5), 67.9 (C_2), 68.4 (C_3), 72.3 (C_4), 90.2 (C_1), 167.9, 168.0 and 169.2 (Ac-CO). HRMS,

Found: m/z 295.0482. Calcd for $C_{10}H_{15}O_8S$ (M-OAc): 295.0476.

1,2,3-Tri-*O*-acetyl-4-*O*-*p*-tolylsulfonyl-α-D-lyxopyranose (18b) and 1,2,3-Tri-*O*-acetyl-4-*O*-*p*-tolylsulfonyl-D-arabinopyranose (17b). A mixture of **18a** (276 mg, 1 mmol, α/β=9/1) and *p*-toluensulfonyl chloride (570 mg, 3 mmol) in dry pyridine (12 ml) was heated at 70 °C under a nitrogen atmosphere with stirring for 17 h. The reaction mixture was cooled, and poured slowly into cold water (20 ml). The solution was extracted with dichloromethane, and the extract was washed with water. After dried over $MgSO_4$, the solvent was evaporated in vacuo, and the product **18b** was isolated through a preparative TLC (silica gel/$CHCl_3$), 259 mg, 60% yield. Referring to ^{13}C NMR, the product was pure α-**18b**. For α-**18b**: GC-MS, m/z (rel intensity) 430 (M^+, 0.13), 371 (6.0), 282 (18.0), 269 (11.0), 215 (37.8), 173 (68.7), 155 (100), 91 (100). ^1H NMR ($CDCl_3$), δ=1.90—2.12 (9H, s, Ac-Me), 3.66—4.09 (2H, m, H_5, $H_{5'}$), 4.79—5.09 (1H, m. H_4), 5.13—5.35 (2H, m, H_2, H_3), 5.93 (1H, d, J=2.3 Hz, H_1), 7.36 and 7.80 (4H, ABq, J=8.3 Hz, Ar), 2.44 (3H, s, Ar-Me). ^{13}C NMR ($CDCl_3$) δ=21.5 (Ar-Me), 61.9 (C_5), 67.6 (C_2), 68.4 (C_3), 72.5 (C_4), 90.2 (C_1), 127.7, 129.8, 133.3, 145.1 (Ar), 169.2 and 169.5 (Ac-CO). HRMS, Found: m/z 430.0956. Calcd for $C_{18}H_{22}O_{16}S$ (M): 430.0934.

In the same way, tosylation of **17a** (172 mg, α/β=1/1) was carried out to give the product **17b** (149 mg, 56% yield) after the chromatograph on a silica gel column (ether). Referring to the NMR signals of anomeric protons, the product was an anomeric mixture (α/β=6/4). For **17b**: GC-MS, m/z (rel intensity) 371 (M^+ −OAc, 5.0), 269 (19.8), 215 (64.7), 172 (47.0), 155 (100), 91 (95.7). ^1H NMR ($CDCl_3$) δ=1.95—2.11 (9H, s, Ac), 2.45 (3H, s, Ar-Me), 3.53—4.11 (2H, m, H_5, $H_{5'}$), 4.90—5.31 (3H, m, H_2, H_3, H_4), 5.62 (3/5H, d, J=6.6 Hz, H_1 of α anomer), 6.31 (2/5H, d, J=3.2 Hz, H_1 of α anomer), 7.35 and 7.80 (4H, ABq, J=8.3 Hz, Ar). ^{13}C NMR ($CDCl_3$) δ=20.3—20.7 (Ac-Me), 62.6 and 63.5 (C_5), 66.2 and 66.7 (C_2), 67.6 and 69.5 (C_3), 73.2 and 75.1 (C_4), 89.9 and 91.7 (C_1) 127.6—145.1 (Ar), 168.6—170.2 (Ac-CO). Found: C, 50.30; H, 5.16%. Calcd for $C_{18}H_{22}O_{16}S$: C, 50.22; H, 5.15%.

1,2-Di-*O*-acetyl-3,4-anhydro-β-L-ribopyranose (19). To a solution of **18b** (α/β=9/1, 101 mg, 0.23 mmol) in methanol (10 ml) was added a methanol solution of NaOMe (0.35 M, 2 ml) dropwise at 0 °C with stirring. After being neutralized with dil HCl, the solution was concentrated to dryness in vacuo. The residue was treated with acetic anhydride (2 ml) and dry pyridine (5 ml), and the solution was concentrated in vacuo. The product was extracted with $CHCl_3$, and the extract was dried over $MgSO_4$. After evaporating the solvent, the product β-**19** was isolated on a preparative TLC (silica gel/ether) in 53% yield 27 mg. For β-**19**: IR (neat) ν_{max} 1740 (acetate), 1240, 895, and 835 (oxirane). GC-MS, m/z (rel intensity) 157 (M^+ −OAc, 12.7), 128 (14.1), 115 (100), 97 (10.2), 89 (39.1), 73 (48.1). ^1H NMR ($CDCl_3$) δ=2.10 and 2.16 (6H, s×2, Ac), 3.31—3.46 (1H, m, H_4), 3.63 (1H, dd, $J_{3,2}$=3.4 and $J_{3,4}$=4.5 Hz, H_3), 4.25 and 4.30 (2H, ABq, H_5, $H_{5'}$),4.97 (1H, dd, $J_{2,1}$=4.5 and $J_{2,3}$=3.4 Hz, H_2), 5.77 (1H, d, $J_{1,2}$=4.5 Hz, H_1). ^{13}C NMR ($CDCl_3$) δ=50.1 and 51.4 (oxirane), 60.7 (C_5), 67.6 (C_2), 89.7 (C_1).

Iron(III) Chloride-Catalyzed Photoreaction of D-Fructose (10). The photoreaction of D-fructose (1.1 g, 6.1 mmol) was carried out under the same conditions as described for D-glucose except shortening the irradiation time to 5 h. After treating with acetic anhydride (15 ml, 159 mmol) the crude sample was distilled to give **11a** as an oil, bp 150—153 °C (0.6 mmHg) 870 mg, 52% yield. The following spectroscopic data were very close to those of γ-ribonolactone triacetate.[7] For **11a**: IR (neat) ν_{max} 1796 (γ-lactone), 1738 cm^{-1} (acetate). GC-MS m/z (rel intensity) 275 (M^+ +1, 13.8), 232 (10.4), 201 (14.0), 172 (23.8), 154 (48.0), 128 (100), 115 (96.0), 100 (80.6), 86 (79.3). ^1H NMR ($CDCl_3$) δ=2.03—2.17 (9H, s×3 Ac), 4.31 (1H, dd, $J_{5',4}$=3.6 and $J_{5',5}$=8.5 Hz, $H_{5'}$), 4.48 (1H, dd, $J_{5,4}$=3.8 and $J_{5,5'}$=8.5 Hz, H_5), 4.60 (1H, ddd, $J_{4,3}$=0.9, $J_{4,5}$=3.8 and $J_{4,5'}$=3.6 Hz, H_4), 5.39 (1H, d, $J_{2,3}$=4.9 Hz, H_2), 5.61 (1H, dd, $J_{3,2}$=4.9 and $J_{3,4}$=0.9 Hz, H_3). ^{13}C NMR ($CDCl_3$) δ=20.3, 20.5 and 20.7 (Ac-Me), 62.2 (C_5), 72.4 and 72.7 (C_2, C_3), 77.5 (C_4) 170.2 (C_1), 168.3, 169.4 and 169.9 (Ac-CO).

Iron(III) Chloride-Catalyzed Thermal Reaction of D-Fructose(10) and D-Glucose (1). A pyridine solution (50 ml) of **10** (500 mg, 2.8 mmol) and $FeCl_3 \cdot 6H_2O$ (750 mg, 2.8 mmol) was stirred for 24 h at room temperature while oxygen gas was bubbled through. The solution was treated with acetic anhydride and worked up in the same way as described for the photoreaction. The product **11a** was obtained through a column chromatography (silica gel/$CHCl_3$) 380 mg, 50% yield.

The thermal reaction of **1** (1.2 g, 6.7 mmol) was performed by refluxing the same pyridine solution as that used for the photoreaction. Treatment with acetic anhydride gave an oil (635 mg), which showed two peaks on a GLC analysis with relative ratio of 6:4. The major component was isolated through a column chromatography (silica gel/hexane-ethyl acetate (1 : 1)), and was shown to be identical (GC-MS, NMR, IR) with **11a** (289 mg, 13% yield). Although the other component was not completely freed from **11a**, it was identified as **11b** from the following spectroscopic data obtained by subtracting the data of **11a** from those of the mixture. For **11b**: IR (neat) ν_{max} 1799 (γ-lactone), 1740 and 1736 cm^{-1} (esters). GC-MS: m/z (rel intensity) 261 (M^+ +1, 9.7), 218 (11.9), 201 (16.3), 128 (100), 99 (57.4), 69 (76.9). ^1H NMR ($CDCl_3$) δ=2.02—2.12 (6H, s, Ac), 4.09—4.44 (3H, m, H_4, H_5), 5.09—5.59 (2H, m, H_2, H_3), 8.10 (1H, s, CHO).

Iron(III) Chloride-Catalyzed Photoreaction of D-Arabinose (6). The photoreaction of D-arabinose (**6**, 1.28 g, 8.5 mmol) and the subsequent acetylation was performed in the same way as described for D-glucose (**1**). The crude product gave two fractions by distillation. The lower boiling fraction, bp 135—140 °C (0.15 mmHg), 98 mg, 5% yield, was **15b**. For **15b**: GC-MS, m/z (rel intensity) 173 (M^+ −OAc, 11.7), 127 (20.9), 101 (29.6), 85 (100). ^1H NMR ($CDCl_3$) δ=1.95—2.20 (6H, s, Ac), 3.81—4.52 (2H, m, H_4, $H_{4'}$), 5.05—5.70 (2H, m, H_2, H_3), 5.72 (1/3H, s, H_1 of β anomer),6.05 (2/3H, d, J=2.1 Hz, H_1 of α anomer), 7.70 and 7.95 (1H, s×2, CHO).

The higher boiling fraction, bp 148—152 °C (0.15 mmHg), was identified as D-arabinose tetraacetate (**5b**, 1.7 g, 63% yield) by comparing the NMR and mass spectra with those of the authentic sample.

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