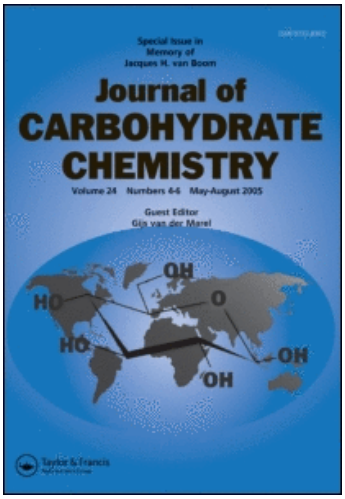

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Younosuke Araki[a]; Naoki Kobayashi[a]; Kazuko Watanabe[a]; Yoshiharu Ishido[a]
[a] Department of Chemistry, Faculty of Science, Tokyo Institute of Technology, Tokyo, 152, Japan

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SYNTHESIS OF GLYCOSYL CYANIDES AND C-ALLYL GLYCOSIDES BY THE USE OF GLYCOSYL FLUORIDE DERIVATIVES[1]

Younosuke Araki, Naoki Kobayashi, Kazuko Watanabe, and Yoshiharu Ishido*

Department of Chemistry, Faculty of Science,
Tokyo Institute of Technology,
O-okayama, Meguro-ku, Tokyo 152, Japan

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ABSTRACT

A treatment of 2,3,5-tri-O-benzyl-β-D-ribofuranosyl fluoride (**1**) with cyanotrimethylsilane in the presence of boron trifluoride diethyl etherate gave 2,3,5-tri-O-benzyl-α- (**2α**) and -β-D-ribofuranosyl (**2β**) cyanide in 46.2% and 46.6% yields, respectively. Confirmation of the corresponding isocyano isomer (**3**) formation and its conversion into **2** under boron trifluoride catalysis at -78°C made it possible to deduce that both **2α** and **2β** were produced by way of **3** which was formed preponderantly in the initial stage of the reaction. On the other hand, the reaction of 2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyl fluoride (**4**) with cyanotrimethylsilane in diethyl ether by the use of boron trifluoride diethyl etherate (0.05 mol. equiv.) gave 2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyl cyanide (**5α**), 2,3,4,6-tetra-O-benzyl-α- (**6α**), and -β-D-glucopyranosyl isocyanide (**6β**) as a 30:61:9 mixture (94% yield) but that in dichloromethane by the use of the catalyst (1.0 mol. equiv.) gave **5α** (85% yield) as a sole product.

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The reactions of 1 and of 4 with allyltrimethylsilane under the same catalysis afforded C-allyl 2,3,5-tri-O-benzyl-α-D-ribofuranoside (7)(93.5% yield), and C-allyl 2,3,4,6-tetra-O-benzyl-α- (8α)(71.8% yield) and -β-D-glucopyranoside (8β)(22.4% yield), respectively.

INTRODUCTION

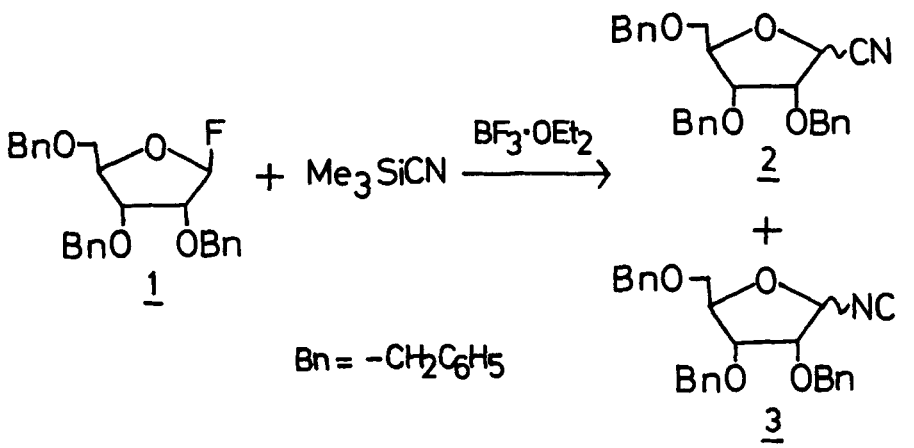
Since Mukaiyama et al.[2,3] demonstrated the excellent utility of glycosyl fluorides as glycosyl donors and the high stereoselectivity in their Lewis acid-catalyzed coupling reaction with alcohols, a number of papers have been appeared on glycosylation through glycosyl fluorides[4-10,16] and novel preparative procedures for glycosyl fluoride derivatives.[3,4,11-18] Moreover, we reported highly stereoselective C-acetonylation and β-D-ribofuranosyl β-D-ribofuranoside formation reaction by the use of a ribofuranosyl fluoride derivative,[16,17] which showed further the utility of glycosyl fluorides in glycosylation. Successively, we now report Lewis acid-catalyzed coupling reactions of a glycosyl fluoride derivative with cyanotrimethylsilane and with allyltrimethylsilane.

A large number of C-glycosyl compounds have been reported. These include Aloe emodine glycosides,[19,20] ψ-uridine,[21] and C-nucleoside antibiotics.[21] Synthetic studies on these target compounds have been conducted extensively. Moreover, stereoselective C-glycosylation has been investigated as a potential key-step for the chiral synthesis of biologically active organic natural

products,[22-25] in which silyl organic compounds have been shown to be very useful as glycosyl acceptors.[5,8,22-31]

RESULTS AND DISCUSSION

In our first experiment, boron trifluoride-catalyzed coupling of 2,3,5-tri-O-benzyl-β-D-ribofuranosyl fluoride (1)[16,17] with cyanotrimethylsilane was performed under the conditions, which gave the best results in terms of the yield and stereoselectivity from the reaction of 1 with isopropenyl trimethylsilyl ether, i.e., in the presence of BF_3-OEt_2 (0.05 equiv.) at room temperature[16,17] for 30 min. These conditions gave 2,3,5-tri-O-benzyl-D-ribofuranosyl cyanide (2) in a high yield (See Entry 1, Table 1) but with



very poor stereoselectivity. The ratio of the α-anomer (2α) to the β-anomer (2β) was approximately 1 : 1 after separation by column chromatography. Both of these anomers gave an IR absorption band at 2230 cm^{-1} (very weak), charac-

TABLE 1

Reactions of 2,3,5-Tri-O-benzyl-β-D-ribofuranosyl Fluoride (1) with Cyanotrimethylsilane[a]

Entry	Solvent	Reaction temperature	Reaction time	$BF_3 \cdot OEt_2$ (mol. equiv.)	Yield (%) of 2	(α : β)[b]	3
1	Et_2O	room temp.	30 min	0.05	92.8	(1:1.01)	trace
2	CH_2Cl_2	room temp.	12 min	0.05	94.5	(1:1.31)	trace
3	CH_2Cl_2	-22.5°C	5 h	0.05	86.9 (2 + 3)		
4	CH_2Cl_2	-78°C	5 h	0.05	91.3 (2 + 3)		
5	CH_3CN	room temp.	30 min	0.05	82.1	(1:1.42)	---
6	CH_3CN	-40°C	20 min	0.05	87.2	(1:1.81)	---
7	CH_3NO_2	room temp.	30 min	0.05	96.4	(1.22:1)	trace
8	CH_3NO_2	-22.5°C	5.5 h	0.05	~100	(1.16:1)	trace
9	THF[c]	room temp.	5 d	0.05	a mixture (1 + 2 + 3)		
10	THF	-78°C	1.25 h	0.15	no reaction		

[a] All of the reactions were performed by the use of 1 (100 mg, 0.237 mmol), cyanotrimethylsilane (0.07 mL, 0.525 mmol, 2.2 mol. equiv.), and 4A molecular sieves (ca. 1 g) in a solvent (2 mL).
[b] Proportion of the anomers was calculated based on their weight isolated through column chromatographic separation.
[c] Tetrahydrofuran.

teristic of the nitrile group, and at 2120 cm^{-1} (weak but sharp), characteristic of the isonitrile group; the latter absorption showed that these anomers contained trace amounts of isonitrile isomers (3α and 3β). Their presence also was confirmed by TLC analysis. Such poor stereoselectivity in this reaction might arise from anomerization during the course of the reaction. The reaction was monitored by TLC as a function of time but no change was detected in the anomer proportion. Moreover, respective treatments of isolated 2α and 2β in diethyl ether in the presence of boron trifluoride diethyl etherate at room temperature for 7 days resulted in no interconversion. These results suggest to us that the reaction does not involve anomerization under the conditions used. This finding is different from that of C-acetonyl 2,3,5-tri-O-benzyl-D-ribofuranoside,[16,17] which anomerized under these conditions. We have further examined this reaction in other solvents (See Entries 2 - 10, Table 1). The reactions in dichloromethane, acetonitrile, and nitromethane were found to be effective (Entries 2 - 8), but that in tetrahydrofuran left a considerable amount of the starting material unchanged (Entry 9). It was of interest that the reaction in dichloromethane, conducted at a lower temperature, gave 3 as a main product (Entries 3 and 4). It should be noted, however, that 3 is susceptible to isomerization into 2 under ordinary conditions as well as on separation by column chromatography and also is subject to decomposition and anomerization. Therefore, the separation

of a mixture of 2 and 3 was done by carrying out the work-up after the reaction and the chromatographic separation as quickly as possible. The ^{1}H NMR spectrum of the crude mixture barely allowed the estimation of the proportion of 3 as approximately 60% but with large a error.[32] Thus, the formation of a glycosyl isocyanide in the reaction of a glycosyl donor with cyanotrimethylsilane was confirmed for the first time. Product 3 is unstable and susceptible to isomerization into 2 as well as anomerization. Compound 2, in contrast, is stable and not susceptible to isomerization or anomerization. Following this reaction by TLC[33] suggests the following sequence of events. The isocyano compound 3 was initially produced as the kinetically controlled product by the reaction of 1 with cyanotrimethylsilane, but 3 was isomerized into the thermodynamically controlled cyano compound 2. Since compound 2 might be produced through a two- or three-step sequence of reactions, very poor stereoselectivity could result. The high reactivity of 1 made it possible to perform the reaction under very mild conditions and made it possible to isolate 3 prior to much isomerization into 2. Reaction did not take place when milder conditions were used (Entry 10). A rationale for preferred formation of 3 under mild conditions could be based on the following information. It has been reported that cyanotrimethylsilane is in equilibration with isocyanotrimethylsilane[34], which allows the ambident nucleophilic character of cyanotrimethylsilane, similar

to that of metal cyanides, to be evident. The reactions of glycosyl bromide or chloride derivatives with mercuric cyanide gave the corresponding glycosyl cyanide[35,36] and those with silver cyanide the corresponding glycosyl isocyanide derivatives.[37,38] According to Hard-Soft-Acid-Base theory, a reaction center in an S_N1 process (carbenium ion) is harder than that in the S_N2 reaction, and the center tends to react with a harder atom of an ambident nucleophile.[39] The reaction of an alkyl halide, for instance, with silver cyanide, proceeds via an S_N1-like mechanism, in which the alkyl halide is susceptible to attack by the harder nitrogen atom to give the corresponding alkyl isocyanide.[40,41] In previous papers,[16,17] incidentally, we have reported the boron trifluoride-catalyzed coupling reaction of 1 with isopropenyl trimethylsilyl ether which was deduced to proceed via S_N1 mechanism based on the predominant formation of a C-glycosyl compound with the same configuration as a kinetically controlled product starting from either 1 or its α-anomer. Among the reactions at a lower temperature, the amounts of isocyano compound 3 formed in acetonitrile and in nitromethane were lower (Entries 6 and 8) than that in dichloromethane (Entries 3 and 4). In acetonitrile and nitromethane, the resulting carbenium ion was solvated, thus to decreasing its hardness. Particularly, entries 5 and 6 show a conspicuous difference in the reactions in acetonitrile compared to those in other solvents; i.e., lower yields of 2, higher proportions of 2β to 2α, and no detection of 3. A significant solvent effect of

acetonitrile has recently been reported to reverse the stereoselectivity of tetrafluorosilane-catalyzed glycosidation with a glycosyl fluoride derivative in diethyl ether;[8] also, an interesting participation of acetonitrile in the glycosylation reaction of glycosyl trichloroacetimidates has been reported.[42] These aspects of the solvent effect are of considerable interest.

Subsequently, the reaction of 2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyl fluoride (**4**) with cyanotrimethylsilane was performed; the results thus obtained and the conditions used are summarized in Table 2. The reactions proceeded smoothly and quickly to give 2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyl cyanide (**5α**), isocyanide isomer (**6α**), and the corresponding β-isomer (**6β**) in high yields (Entry 1). When the reaction time was extended to 60 min (Entry 2), there was a preponderant formation of the isocyano compound **6** in the initial stages but it isomerized into the cyano compound **5** with the passage of time. Such a trend also was the case in the reaction of **1** but since **6** is comparatively more stable than **3** and not so susceptible to isomerization or decomposition during the column chromatographic separation, it might have been possible to isolate some **6α** in addition to **6β**. It was interesting that increasing the amount of boron trifluoride diethyl etherate from 0.05 mol. equiv. to 1.0 mol. equiv. resulted in the highly stereoselective formation of **5α** in a high yield (Entry 3). The product **6β** probably contains no

TABLE 2

Reactions of 2,3,4,6-Tetra-O-benzyl-α-D-glucopyranosyl Fluoride (**4**) with Allyltrimethylsilane[a]

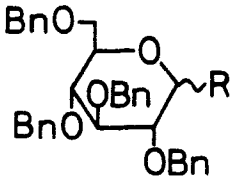
Entry	Solvent	$BF_3 \cdot OEt_2$ (mol.equiv.)	Reaction time (min)	Yield (%) of products	Proportion of products
1	Et_2O	0.05	5	94	**5α**: **6α**: **6β** = 30:61:9[b]
2	Et_2O	0.05	60	75	**5α**: **6α**: **6β** = 48:35:17[b]
3	CH_2Cl_2	1.0	12	85	**5α**

[a] All of the reactions were performed by the use of **4** [137 mg(0.25 mmol) for Entry 1, 163 mg (0.30 mmol) for Entry 2, and 100 mg (0.18 mmol) for Entry 3] in a solvent (0.75 mL for Entry 1, 0.9 mL for Entry 2, and 2 mL for Entry 3) under nitrogen atmosphere at room temperature.

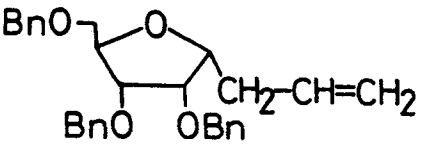
[b] Compound **6β** and a part of **6α** were isolated, and **5α** was obtained as a mixture with **6α**; the proportion of the products **5α** and **6α** was calculated from the ^1H NMR spectra, and the total proportion was obtained by the addition of the amount of isolated products.

5β, based on the result described in Entry 3 and the observation that the cyano compound 2 was not susceptible to anomerization at all, although slight contamination by 5β is impossible to detect since the specific absorption band of cyano group is usually very weak and ^{1}H NMR signals of 5β[38] are concealed by those of 6β.

The final reactions to be considered were those of 1 and 4 with allyltrimethylsilane. Treatment of 1 with



4 : R = α-F
5 : R = −CN
6 : R = −NC
8 : R = $-CH_2-CH=CH_2$



7

allyltrimethylsilane (2 mol. equiv.) in the presence of boron trifluoride diethyl etherate (0.05 mol. equiv.) in dichloromethane under nitrogen atmosphere at room temperature for 30 min gave C-allyl 2,3,5-tri-O-benzyl-α-D-ribofuranoside (7) in 93.1% yield. Treatment of the α-anomer of 1 in the same way gave 7 in 93.4% yield. Therefore, these results also suggest that the reaction may proceed via an S_N1 mechanism. Moreover, an attempt at anomerization of

7 thus obtained was unsuccessful in contrast to the corresponding C-acetonyl α-D-ribofuranoside.[16,17]

Similar treatment of 4 with allyltrimethylsilane (2 mol. equiv.) in the presence of boron trifluoride diethyl etherate (1 mol. equiv.) at room temperature for 25 min gave C-allyl 2,3,4,6-tetra-O-benzyl-α- (8α) and -β-D-glucopyranoside (8β) in 71.8% and 22.4% yields, respectively. Nicolaou et al.[5] also reported the reactions of an anomeric mixture of 2,3,4,6-tetra-O-benzyl-D-glucopyranosyl fluorides with cyano- and with allyltrimethylsilane recently but no details were given. These workers did not report isocyano compound 6 from reaction with cyanotrimethylsilane.

In conclusion, glycosyl fluorides were confirmed to be quite reactive under Lewis acid-catalysis and to be useful as glycosyl donors with high stereoselectivity.

EXPERIMENTAL

General Procedures. Melting points were determined by a Yanagimoto Micro-Melting-Point apparatus and are uncorrected. Cyanotrimethylsilane and allyltrimethylsilane were purchased from Aldrich Chem. Co. Solvents were purified and dried according to the usual procedures. 2,3,5-Tri-O-benzyl-β-D-ribofuranosyl fluoride (1)[16-18] and 2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyl fluoride (4)[18] were prepared according to our reported

procedures by the use of 1:1 adducts of hexafluoropropene with diethylamine. Column chromatography was conducted by the flash chromatography technique. ^{1}H NMR spectra were recorded either on a Varian T-60, a JEOL JNM-FX200, and/or a Nicolet NT-360 spectrometer, and ^{13}C NMR spectra were taken on a JEOL JNM-FX200 spectrometer. All spectra were run in deuteriochloroform with tetramethylsilane as the internal standard. IR spectra were determined with a Hitachi 285 spectrophotometer and specific rotations were with a JASCO DIP-4 apparatus.

2,3,5-Tri-O-benzyl-α- (2α) and -β-D-ribofuranosyl Cyanide (2β). Under nitrogen atmosphere, anhydrous diethyl ether (2 mL) was added through a syringe into a 50 mL round-bottomed flask in which **1** (100 mg, 0.24 mmol) and 4A molecular sieves (1 g) were put in advance. To the resulting mixture at room temperature, cyanotrimethylsilane (0.07 mL, 0.53 mmol, 2.2 mol. equiv.), was added and, after stirring for 30 min, boron trifluoride diethyl etherate (1.5 μL, 0.012 mmol, 0.05 mol. equiv.) also was introduced, after which the mixture was stirred for 30 min. The resulting mixture was quenched with saturated aqueous sodium bicarbonate and, after filtration, the filtrate was extracted with dichloromethane (2 mL x 6). The organic layers were combined and dried over anhydrous magnesium sulfate. After filtering off the desiccant, the organic solution was evaporated to a syrup, which was then subjected to chromatographic separation on a column of

the silica gel (d: 2.8 cm, length: 10 cm) by the use of 40:1 benzene - ethyl acetate to give 2α (47.0 mg, 46.2% yield) and 2β (47.5 mg, 46.6% yield)[2α/2β = 1/1.01](See Entry 1 in Table 1). Moreover, it was shown by IR spectroscopy that both isomers thus obtained contained a trace amount of the corresponding isocyano compounds (see Results and Discussion).

Compound 2α was syrup, $[\alpha]_D$ = +63.24° (c 1.0, chloroform)[lit.[28] +70° (c 1, chloroform)], ^{1}H-NMR (360 MHz): δ 3.33 (1H, ddd, $J_{3,4}$ 3.97 Hz, $J_{4,5}$ 3.20 Hz, $J_{4,5'}$ 3.12 Hz,H-4), 3.45 (1H, dd, $J_{5,5'}$ 10.9 Hz, H-5), 3.54 (1H, dd, H-5'), 3.99 (1H, dd, $J_{2,3}$ 5.12 Hz, H-3), 4.16 (1H, dd, $J_{1,2}$ 5.98 Hz, H-2), 4.40 - 4.74 (6H, m, $PhCH_2$ x 3), 4.73 1H, d, H-1), and 7.31 - 7.33 (15H, bs, C_6H_5 x 3), IR: ν_{CN} 2230 cm^{-1} (w) and ν_{NC} 2120 cm^{-1} (w).

Anal. Calcd for $C_{27}H_{27}O_4N$: C, 75.50; H, 6.34; N, 3.26. Found: C, 75.56; H, 6.38; N, 3.00.

Compound 2β was syrup, $[\alpha]_D$ = +10.0° (c 1.0, chloroform)[lit.[28] +12° (c 1, chloroform)], ^{1}H-NMR (360 MHz): δ 3.50 (1H, dd, $J_{4,5}$ 3.75 Hz, $J_{4,5'}$ 10.9 Hz, H-5), 3.57 (1H, dd, $J_{4,5'}$ 3.4 Hz, H-5'), 4.05 (1H, dd, $J_{2,3}$ 4.87 Hz, $J_{3,4}$ 4.57 Hz, H-3), 4.30 (1H, dd, $J_{1,2}$ 5.2 Hz, H-2), 4.36 (1H, ddd, H-4), 4.47 - 4.60 (6H, m, $PhCH_2$ x 3), 4.62 (1H, d, H-1), and 7.28 - 7.34 (15H, bs, C_6H_5 x 3), IR: ν_{CN} 2230 cm^{-1} (w) and ν_{NC} 2120 cm^{-1} (w).

Anal. Calcd for $C_{27}H_{27}O_4N$: C, 75.50; H, 6.34; N, 3.26. Found: C, 75.56; H, 6.41; N, 3.11.

^{1}H-NMR Spectra of 2,3,5-Tri-O-benzyl-α-(3α) and -β-D-ribofuranosyl Isocyanide (3β) The reactions performed under the conditions shown in Entry 3 or 4 of Table 1, followed by the same work-up as described above, gave mixtures of 2α and 3α and 2β and 3β. Substitution of the proton signals of 2α and 2β respectively from the spectra of the above two mixtures made it possible to determine the spectra of 3α and 3β to be as follows:

^{1}H-NMR of 3α (360 Mhz): δ 4.11 (1H, dd, $J_{1,2}$ 2.3 Hz, $J_{2,3}$ 4.2 Hz, H-2), 4.19 (1H, dd, $J_{3,4}$ 6.2 Hz, H-3), 4.30 (1H, ddd, $J_{4,5}$ 4.0 Hz, $J_{4,5'}$ 3.1 Hz, H-4), 4.57 (1H, dd, $J_{5,5'}$ 11.0 Hz, H-5), 4.65 (1H, dd, H-5'), and 5.13 (1H, d, H-1).

^{1}H-NMR of 3β (360 MHz, C_6D_6 - TMS): δ 3.06 (1H, dd, $J_{4,5}$ 2.9 Hz, $J_{5,5'}$ 10.8 Hz, H-5), 3.17 (1H, dd, $J_{4,5'}$ 3.3 Hz, H-5'), 3.63 (1H, t, $J_{1,2}$ 5.2 Hz, $J_{2,3}$ 5.7 Hz, H-2), 3.85 (1H, dd, $J_{3,4}$ 2.9 Hz, H-3), and 4.87 (1H, d, H-1); the δ value of the H-4 signal could not be determined.

2,3,4,6-Tetra-O-benzyl-α-D-glucopyranosyl Cyanide (5α), 2,3,4,6-Tetra-O-benzyl-α- (6α), and -β-D-glucopyranosyl Isocyanide (6β). The reactions of 4 with cyanotrimethylsilane were performed under the conditions described in Table 2, in which the results thus obtained are shown in Entries 1 - 3. The reaction in Entry 1 gave 6α (18 mg), a mixture of 6α and 5α (101 mg), and 6β (12 mg), and that in Entry 2 6α (11 mg), the mixture of 6α and 5α (92 mg), and 6β (21 mg).

Compound 5α was syrup, $[\alpha]_D^{28}$ +31.5° (c 0.75, chloroform) [lit.[38] +36.3° (c 5.3, chloroform)], ^{1}H-NMR (200 MHz): δ 3.31 - 4.06 (6H, m, H-2, 3, 4, 5, 6, and 6'), 4.46 - 4.93 (9H, m, H-1 and $PhCH_2$ x 4), and 7.15 - 7.32 (20H, m, C_6H_5 x 4); and (200 MHz, CD_3COCD_3): δ 5.25 (1H, d, $J_{1,2}$ 4.7 Hz, H-1) [lit.[38] ^{1}H-NMR (100 MHz, CD_3COCD_3): δ 5.21(1H, d, $J_{1,2}$ 4.2 HZ, H-1)], IR: no specific absorption bands for cyano and isocyano groups have been observed. Incidentally, a glycopyranosyl cyanide derivative has been reported to give cyano absorption in the IR[43].

Compound 6α was syrup, ^{1}H-NMR (360 MHz): δ 3.58 (1H, q, $J_{1,2}$ 4.5 Hz, $J_{2,3}$ 9.3 Hz, H-2), 3.63 - 3.90 (5H, m, H-3, 4, 5, 6, and 6'), 4.43 - 4.97 (8H, m, $PhCH_2$ x 4), 5.11 (1H, d, H-1), and 7.34 - 7.25 (20H, m, C_6H_5 x 4); and (60 MHz, CD_3COCD_3): δ 5.62 (1H, d, $J_{1,2}$ 4 Hz, H-1) [lit.[38] ^{1}H-NMR (100 MHz, CD_3COCD_3 -TMS): δ 5.63 (1H, d, $J_{1,2}$ 3.6 Hz, H-1)], IR: ν_{NC} 2120 cm^{-1} (lit.[38] ν_{NC} 2124.5 cm^{-1}).

Compound 6β was syrup, ^{1}H-NMR (360 MHz): δ 3.42 (1H, bd, $J_{4,5}$ 9 Hz, $J_{5,6} = J_{5,6'}$ 3 Hz, H-5), 3.60 (1H, t, $J_{2,3} = J_{3,4}$ 9 Hz, H-3), 3.65 (1H, t, H-4), 3.67 (1H, dd, $J_{6,6'}$ 10 Hz, H-6), 3.72 (1H, dd, H-6'), 3.78 (1H, dd, $J_{1,2}$ 10 Hz, H-2), 4.06 (1H, d, H-1), 4.78 - 4.94 (8H, m, $PhCH_2$ x 4), and 7.27 - 7.33 (20H, m, C_6H_5 x 4); and (60 MHz, CD_3COCD_3): δ 4.20 - 5.00 (9H, m, H-1 and $PhCH_2$ x 4)(lit.[38] ^{1}H-NMR (100 MHz, CD_3COCD_3 - TMS): δ

4.5 - 5.0 (9H, m, H-1 and $PhCH_2$ x 4), IR: ν_{NC} 2138 cm^{-1} (lit.[38] ν_{NC} 2142.5 cm^{-1}).

C-Allyl 2,3,5-Tri-O-benzyl-α-D-ribofuranoside (7). Compound 1 (100 mg, 0.24 mmol) was subjected to the reaction with allyltrimethylsilane as described in the text, followed by the same work-up as has been described in the previous experiments, to give 7 (108.4 mg, 93.1% yield), m.p. 58 - 59°C (from hexane), $[\alpha]_D^{26}$ +40.0° (c 0.89, chloroform), ^{1}H-NMR (360 MHz, CD_3COCD_3) [cf. $-C(1')H_2-C(2')H=C(3')H_2$]: δ 2.51 (2H, ddt, $J_{1',2'}$ 7.3 Hz, $J_{1,1'}$ 7 Hz, $J_{1',3'}$ 1.1 Hz, $J_{1',3''}$ 1.5 Hz, H-1'), 3.51 (1H, dd, $J_{5,5'}$ 11.0 Hz, $J_{4,5}$ 3.2 Hz, H-5), 3.63 (1H, dd, $J_{4,5'}$ 3.5 Hz, H-5'), 3.97 (1H, t, $J_{1,2}$ 3.5 Hz, $J_{2,3}$ 4.2 Hz, H-2), 4.05 (1H, dt, H-1), 4.09 (1H, dd, $J_{3,4}$ 6.9 Hz, H-3), 4.21 (1H, dt, H-4), 4.46 - 4.85 (6H, m, $PhCH_2$ x 3), 5.03 (1H, ddt, $J_{2',3'}$ 10.5 Hz, $J_{3',3''}$ 2 Hz, H-3'), 5.09 (1H, ddt, $J_{2',3''}$ 17.5 Hz, H-3''), 5.79 (1H, ddt, H-2'), and 7.22 - 7.40 (15H, m, C_6H_5 x 3).

Anal. Calcd for $C_{29}H_{32}O_4$: C, 78.35; H, 7.25. Found: C, 78.24; H, 7.34.

C-Allyl 2,3,4,6-Tetra-O-benzyl-α- (8α) and -β-D-glucopyranoside (8β). Compound 4 (100 mg, 0.18 mmol) was subjected to the reaction with allytrimethylsilane under the conditions as described in the text, followed by the same work-up as has been described in the previous experiment, to give 8α (75 mg, 71.8% yield) and 8β (23 mg, 22.4% yield).

Compound 8α, m.p. 64.0 - 64.5°C (from hexane), $[\alpha]_D^{28}$ +38.9° (c 1.1, chloroform)(lit.[23] m.p. 59 - 61 °C, $[\alpha]_D$ +39.0°; lit.[30] m.p. 55.5 - 56°C, $[\alpha]_D$ +48.9°, ^{1}H-NMR (200 MHz)[cf. -C(1')H_2-C(2')H=C(3')H_2]: δ 2.44 - 2.49 (2H, m, $J_{1',2'}$ 7.6 Hz, H-1'), 3.06 - 3.80 (6H, m, H-2, 3, 4, 5, 6, and 6'), 4.04 - 4.18 (1H, m, H-1), 4.42 - 4.96 (8H, m, $PhCH_2$ x 4), 5.10 (2H, dd, $J_{2',3'}$ 11.0 Hz, $J_{3',3''}$ 20 Hz, H-3' and 3"), 5.70 - 5.92 (1H, m, H-2'), and 7.10 - 7.32 (20H, m, C_6H_5 x 4)[lit.[23] ^{1}H-NMR: δ 2.50 (2H, m, H-1'), 3.55 - 4.12 (6H, m, H-2, 3, 4, 5, 6, and 6'), 4.40 - 4.95 (9H, m, H-1 and $PhCH_2$ x 4), 5.10 (2H, dd, H-3' and 3"), 5.80 (1H, m, H-2'), and 7.10 - 7.40 (20H, m, C_6H_5 x 4)].

Compound 8β, m.p. 89.0 - 90.5°C (from hexane), $[\alpha]_D^{28}$ +18° (c 1.2, chloroform), ^{1}H-NMR (200 MHz)[cf. -C(1')H_2-C(2')H=C(3')H_2]: δ 2.20 - 2.66 (2H, m, $J_{1',2'}$ 7.2 Hz, H-1'), 3.28 - 3.44 (3H, m, H-5, 6, and 6'), 3.46 - 3.80 (3H, m, H-2, 3, and 4), 4.10 (1H, m, H-1), 4.42 - 4.92 (8H, m, $PhCH_2$ x 4), 5.10 (2H, dd, $J_{2',3'}$ 17 Hz, $J_{2',3''}$ 11.0 Hz, H-3', and 3"), 5.70 - 6.02 (1H, m, H-2'), and 7.10 - 7.32 (20H, m, C_6H_5 x 4).

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32 The proportion was estimated by comparing the area ratios of H-1 signal of 2α (4.73 ppm) and of 3α (5.13 ppm) with those of phenyl and methylene proton signals of benzyl groups based on an assumption that the amounts of 2α and 2β were approximately the same.

33 Rf values (4:1 cyclohexane - ethyl acetate): 2α = 3α = 0.28; 2β = 3β = 0.33; and 1 = 0.41; both of the spots of 2 and 3 were detected as dark spots on irradiation with a UV lamp, and, on heating after spraying dilute aqueous sulfuric acid. The former was as a transparent spot and the latter was as a black spot, respectively. The upper edge of the spot of 2 was darkly discolored when the content of 3 was decreased with the passage of time. Thus, we could roughly follow the reaction through TLC.

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