Branched-chain Sugars. IX. Reaction of 3,6-Anhydro-1,2-*O*-isopropylidene-α-D-*ribo*-hexofuranos-3-ulose with Nitromethane or Hydrogen Cyanide[1)]

Ken-ichi SATO, Juji YOSHIMURA, and Chung-gi SHIN*

Laboratory of Chemistry for Natural Products, Faculty of Science, Tokyo Institute of Technology, Meguro-ku, Tokyo 152

**Laboratory of Organic Chemistry, Faculty of Technology, Kanagawa University, Rokkakubashi, Kanagawa-ku, Yokohama 221*

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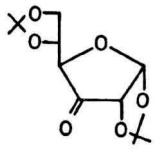
3,6-Anhydro-1,2-*O*-isopropylidene-α-D-*ribo*-hexofuranos-3-ulose (**2**) was converted into 5,6-di-*O*-acetyl-1,2-*O*-isopropylidene-α-D-*ribo*-hexofuranos-3-ulose (**5**) by the protection of the carbonyl function with hydroxylamine, followed by acetylation and removal of the protecting group with chromium(II) acetate. Nitromethane condensation of **2** and **5** at room temperature gave the corresponding 3-nitromethyl derivatives having D-gluco- and D-*allo*-configuration, respectively. The difference in the stereoselectivity was explained by the easiness of isomerization of the initial product to thermodynamically stable epimer, because the reaction temperature was essential to control the selectivity in the same reaction of 1,2 : 5,6-di-*O*-isopropylidene-α-D-*ribo*-hexofuranos-3-ulose. Reaction of **2** with hydrogen cyanide in dry pyridine followed by acetylation gave the corresponding 3,5,6-tri-*O*-acetyl-3-cyano derivative of D-*allo*-type, whereas, the reaction in water gave instantly 3-(hydroxycarbonimidoyl)-1,2-*O*-isopropylidene-α-D-allofuranose 3′,5-lactone, by the participation of the C_5-hydroxyl group.

Up to date, many works have been reported on the nucleophilic reaction of easily available 1,2 : 5,6-di-*O*-isopropylidene-α-D-*ribo*-hexofuranos-3-ulose (**1**),[2-4)] and we also reported on the stereoselectivities of some reactions.[5)] This compound decomposes often to 3,6-anhydro-1,2-*O*-isopropylidene-α-D-*ribo*-hexofuranos-3-ulose (**2**)[6)] during the storage, unless kept at lower temperature in pure state. Although **2** is easily obtained by the partial hydrolysis of **1**,[7)] it is unfavorably formed during the preparation of **1** by the dimethyl sulfoxide oxidation of 1,2 : 5,6-di-*O*-isopropylidene-α-D-glucofuranose, and easily separated from the chloroform solution of the products by extraction with water, sometimes in *ca.* 30% yield. Intramolecular hemiacetal structure of **2**[8)] indicates a diminished reactivity of the carbonyl function, but the hydrogenation[6)] and *p*-nitrophenylhydrazone formation[7)] of **2** were described in literatures.

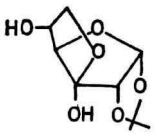
In order to find useful utilizations of **2** as a starting material for the branched-chain sugar synthesis, **2** was converted into 5,6-di-*O*-acetyl-1,2-*O*-isopropylidene-α-D-*ribo*-hexofuranos-3-ulose, and the addition of nitromethane and hydrogen cyanide to both compounds were carried out in this paper. A new evidence on the stereoselectivity of the former reaction and a participation of a neighboring hydroxyl group in the latter reaction are described.

Results and Discussion

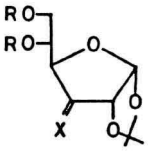
Attempted acetonation of **2** into **1** and the Grignard reaction of **2** gave unsuccessful results, indicating that the intramolecular hemiacetal ring of **2** is fairly stable like that of 2-ketoses. Although much stronger nucleophiles such as nitromethanide anion and cyanide ion are deduced to be reactable with **2**, conversion of **2** into a more reactive 3-ulose derivative having the naked carbonyl group was tried at first. Condensation of **2** with hydroxylamine in aqueous ethanol gave the cor-



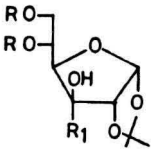
(**1**)



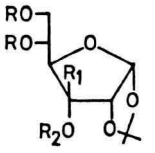
(**2**)



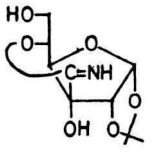
(**3**) R=H, X=NOH
(**4**) R=Ac, X=NOAc
(**5**) R=Ac, X=O



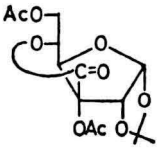
(**6**) R=H, R_1=CH_2NO_2
(**7**) R=Ac, R_1=CH_2NO_2
(**8**) R=H, R_1=CH_2NH_2
(**9**) R=Ac, R_1=CH_2NHAc



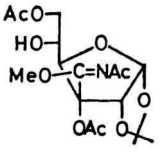
(**10**) R=Ac, R_2=H, R_1=CH_2NO_2
(**11**) R=R_2=H, R_1=CH_2NO_2
(**12**) R=R_2=Ac, R_1=CN
(**16**) R=R_2=H, R_1=COONa



(**13**)



(**14**)



(**15**)

responding oxime derivative (**3**) in 74% yield, and then base-catalyzed acetylation of **3** gave the tri-*O*-acetate (**4**) quantitatively. The NMR spectrum of **4** indicated the presence of both *syn*- and *anti*-forms, but they were not assigned. Treatment of **4** with excess chromium-(II) acetate[9] in tetrahydrofuran–water (9 : 1) at room temperature for 12 h gave successfully the corresponding 3-ulose (**5**) in 85% yield. Tronchet *et al.* synthesized **5** from 3-*O*-benzyl-1,2;5,6-di-*O*-isopropylidene-α-D-glucose *via* four step conversions, and reported that **5** is unstable on TLC.[7]

Reaction of **2** with *aci*-nitro salt of nitromethane in ethanol does not proceeded at −70 °C; however, at room temperature for 30 min a condensation product (**6**) was obtained in 83% yield. The configuration of **6** was determined to be D-*gluco*-type by acetonation of **6** into well known 1,2 : 5,6-di-*O*-isopropylidene-3-(nitromethyl)-α-D-glucofuranose.[10] Base-catalyzed acetylation of **6** gave the corresponding 5,6-di-*O*-acetate (**7**) quantitatively. Hydrogenation of **6** in the presence of palladium–charcoal afforded the 3-*C*-aminomethyl derivative (**8**), which was then converted into the corresponding *N*,*O*-triacetate (**9**) in a good yield. Besides, the nitromethane condensation of **5** under the same conditions as used for **2** gave unexpectedly a different 3-*C*-nitromethyl derivative (**10**) from **7** in 71% yield. These compounds are considered to be 3-epimer to each other, however, there is also the possibility of the inversion at C-4 position[11] under the reaction conditions. Consequently, 1,2 : 5,6-di-*O*-isopropylidene-3-(nitromethyl)-α-D-allofuranose[5,10] was partially hydrolyzed to the corresponding 1,2-*O*-isopropylidene derivative (**11**) quantitatively, and then acetylated. The identity of the di-*O*-acetate obtained and **10** clearly established the 3-epimeric interrelation between **10** and **7**.

Table 1. The predominant epimer produced in the nitromethane condensation of **1** under various conditions[a]

Reaction conditions				Epimer ratio	
Temp (°C)	Time (min)	Solvent[b]	Base[c]	*gluco*	*allo*
−78	30	EtOH	NaOEt	0	1
−78	30	EtOH	Et_3N	0	1
−78	30	THF	Et_3N	0	1
−78	30	Dioxane	Et_3N	0	1
25	3	EtOH	NaOEt	0	1
25	30	EtOH	NaOEt	1	0
25	30	EtOH	Et_3N	1	0
25	30	THF	NaOFt	1	0
25	30	Dioxane	NaOEt	1	0
25	30	THF	Et_3N	1	0
25	30	CH_3NO_2	NaH	1	0
25	[24 h]	Glyme	NaH	0.8	0.2[d]
25	30	DMF	Et_3N	0.8	0.2
25	30	HMPA	HMPA	0	1
25	30	DMSO	Et_3N	0	1

a) The reaction mixture was extracted with chloroform, after neutralization with 60% acetic acid. The configuration and ratio of epimers were estimated from the intensity of H_1-proton signals in the NMR spectrum. b) THF = tetrahydrofuran, DMF = *N*,*N*-dimethylformamide, HMPA = hexamethylphosphoramide, DMSO = dimethyl sulfoxide, Glyme = 1,2-dimethoxyethane. c) The amount of bases used are a slightly excess than the equivalent. d) Cited from the literature, A. Rosenthal, K.-S. Ong, and D. Baker, *Carbohyd. Res.*, **13**, 113 (1970).

In general, the nitromethane condensation of uloses give one epimer or mixture of epimers depending on the reaction conditions.[12] As is seen in Table 1, the reaction temperature is the most essential to control the stereoselectivity of the nitromethane condensation of **1**. This fact implies that the composition of the product is determined by the rate of isomerization of the initial product: kinetically controlled product, to the thermodynamically stable isomer. Thus, the difference of the configuration of the products in the reaction of **2** and **5** should be explained from the free energy difference between the epimers in each case. The kinetic studies will be reported elsewhere.

On the other hand, reaction of **2** with hydrogen cyanide in pyridine at 0 °C for 6 h and successive acetylation of the reaction mixture with acetic anhydride gave the corresponding 3-cyano-tri-*O*-acetate (**12**) in 54% yield. The configuration of **12** was confirmed to be D-*allo*-type by comparison of the NMR spectrum with that of the authentic sample, prepared from the corresponding 5,6-*O*-isopropylidene derivative.[13] Besides, the reaction of **2** with potassium cyanide in water in the presence of sodium hydrogencarbonate at 0 °C gave instantly a crystalline product (**13**) in 66% yield, which shows charateristic IR absorptions at 3300 (C=NH) and 1705 (–O–C=NH) cm^{-1}. From the elemental analysis and the following reactivities, **13** was deduced to be 3-(hydroxycarbonimidoyl)-1,2-*O*-isopropylidene-α-D-allofuranose 3′,5-lactone. On standing in water, **13** changed gradually into the corresponding lactone ($\nu_{C=O}$ 1785 cm^{-1}).[13] When **13** was acetylated with acetic anhydride in pyridine and then the reaction mixture poured into water, known 3,6-di-*O*-acetyl-3-carboxy-1,2-*O*-isopropylidene-α-D-allofuranose 3′,5-lactone (**14**)[13,14] was obtained in 61% yield, whereas treatment of the acetylated product with methanol gave 3,6-di-*O*-acetyl-1,2-*O*-isopropylidene-3-[(acetylimino)methoxymethyl]-α-D-allofuranose (**15**) in 65% yield. The structure of **15** was determined from the analytical values and the absence of the deshielding effect of acetyl group on H_5 proton in the NMR spectrum. Moreover, treatment of **13** with sodium hydrogencarbonate in methanol overnight at reflux temperature gave quantitatively the corresponding carboxylate (**16**) which can be converted into **14** by acetylation with acetic anhydride in a good yield.

Bourgeois reported on the isomerization of the initially formed 3-cyano-1,2 : 5,6-di-*O*-isopropylidene-α-D-allofuranose to the corresponding D-gluco-epimer in the reaction of **1** with hydrogen cyanide.[15] From the fact, it is considered that the kinetically controlled product **12** was simply formed in the same reaction of **2** in pyridine at 0 °C. However, the reaction in water gave **13**, whose formation is attributed to the further participation of a sterically favorable hydroxyl group in the same molecule. The reason for this difference is

ambiguous at present, but the similar participations are known in carbohydrate chemistry.[16,17]

Experimental

All the melting points are uncorrected. The solution were evaporated under diminished pressure at a bath temperature not exceeding 45 °C. Specific rotations were measured in a 0.5 dm tube, with a Carl Zeiss LEP-Al polarimeter. The IR spectra were recorded with a Hitachi Model EPI-G2 spectrometer. The NMR spectra were taken with a JEOL-4H-100 MHz spectrometer, using tetramethylsilane as an internal standard, in deuteriochloroform unless otherwise stated. Chemical shifts and coupling constants were recorded in δ and Hz units, and frequencies in cm^{-1}.

1,2-O-Isopropylidene-α-D-ribo-hexofuranos-3-ulose Oxime (3). To an aqueous ethanol solution (1 : 1, 100 ml) of hydroxylamine prepared from hydroxylamine hydrochloride (1.8 g, 25.9 mmol) and sodium hydroxide (1.10 g, 27.5 mmol) was added the hemiketal **2** (5 g, 22.9 mmol). After standing the reaction mixture at room temperature for 18 h, the solution was concentrated to a half volume, and then extracted with 1-butanol. Evaporation of the butanol solution gave crystals which were recrystallized from ethanol-hexane. Yield, 3.95 g (74%); mp 161—164 °C; $[\alpha]_D^{23}$ +97.2° (*c* 1.3, MeOH); IR: 3400, 3210, and 3125(OH).

Found: C, 46.30; H, 6.38; N, 5.83%. Calcd for $C_9H_{15}NO_6$: C, 46.35; H, 6.48; N, 6.01%.

3-Acetoxyimino-5,6-di-O-acetyl-1,2-O-isopropylidene-α-D-ribo-hexofuranose (4). Base-catalyzed acetylation of **3** with acetic anhydride in the usual manner gave a sirupy product quantitatively. NMR spectrum of the sirup showed the presence of two kind of isomers (*syn*- and *anti*-form) in the ratio of 1 : 1 (H_1 : 6.05 and 5.98). This sirup was used for the next conversion without further identification. IR; 1740 (OAc).

5,6-Di-O-acetyl-1,2-O-isopropylidene-α-D-ribo-hexofuranos-3-ulose (5). A suspension of the above sirup (200 mg, 0.56 mmol) and excess chromium(II) acetate (340 mg, 2 mmol) in tetrahydrofuran–water (9 : 1, 10 ml) was stirred at room temperature for 24 h until the starting material had disappeared on TLC. The reaction mixture was bubbled with air to oxidize excess chromous ion and most of tetrahydrofuran was evaporated. The remaining solution was diluted with water, and then extracted with ether. The ether extract was washed with water, and then evaporated to give a nearly pure sirupy ulose in 85% yield. The NMR spectrum was identical with that of authentic sample: 6.10 (H_1: d, $J_{1,2}$=4.4), 5.26 (H_5: m), 4.53 (H_4: dd, $J_{2,4}$= 1.2, $J_{4,5}$=3.4), 4.45—4.16 (H_2, H_6, $H_{6'}$: m), 2.08 and 2.01 (2×OAc), 1.47 and 1.42 (2×C-CH_3).

1,2-O-Isopropylidene-3-(nitromethyl)-α-D-glucofuranose (6). A solution of **2** (5.0 g, 22.9 mmol) in ethanol (15 ml) was added to a solution of nitromethane (20 ml) and sodium ethoxide (sodium 0.53 g, 23.0 mmol) in ethanol (50 ml) with stirring. The reaction mixture was kept at room temperature for 30 min, neutralized with 60% acetic acid, and then evaporated. A 1-butanol solution (100 ml) of the residue was washed with a small amount of water and then evaporated to give crystals which were recrystallized from ether. Yield, 5.2 g (81.4%), mp 104—105 °C, $[\alpha]_D^{23}$ +57.1° (*c* 0.99, MeOH). IR: 3430 and 3250 (OH), 1540 (NO_2).

Found: C, 43.11; H, 6.14; N, 4.90%. Calcd for $C_{10}H_{17}NO_8$: C, 43.01; H, 6.14; N, 5.02%.

The configuration of this compound was determined by conversion into 1,2 : 5,6-di-*O*-isopropylidene-3-(nitromethyl)-α-D-glucofuranose as follows: a suspension of **6** (1.0 g, 3.6 mmol) and anhydrous copper(II) sulfate (3.0 g) in dry acetone (50 ml) was stirred at 50 °C for 24 h, filtered through active carbon, and the filtrate was evaporated. A chloroform solution of the residue was washed with water and evaporated to give crystals which were recrystallized from ethanol. Yield, 0.82 g (71.4%), mp 139—140 °C, $[\alpha]_D^{23}$ +22.3° (*c* 1.0, $CHCl_3$) [lit,[10] mp 140—141 °C, $[\alpha]_D^{23}$ +22.8° ($CHCl_3$)]. This specimen showed no depression of mp by admixture with an authentic sample.

5,6-Di-O-acetyl-1,2-O-isopropylidene-3-(nitromethyl)-α-D-glucofuranose (7). Base-catalyzed acetylation of **6** with acetic anhydride in the usual manner gave the corresponding di-*O*-acetate quantitatively. Mp 163.5—164.5 °C, $[\alpha]_D^{23}$ +52.6° (*c* 0.5, $CHCl_3$). IR: 3430 (OH), 1745 (OAc), 1560 (NO_2); NMR: 5.97 (H_1: d, $J_{1,2}$=3.8), 5.25 (H_5; oct), 4.62 (H_2: d), 4.62 (H_6: q, $J_{5,6}$=2.5), 4.18 ($H_{6'}$: q, $J_{5,6'}$=5.3, $J_{6,6'}$=12.8), 4.87 and 4.60 (CH_2: ABq $J_{A,B}$=14.8), 4.05 (H_4: d, $J_{4,5}$=8.5), 3.76 (OH, s), 2.10 and 2.06 (2×OAc), 1.52 and 1.34 (2×C-CH_3).

Found: C, 46.28; H, 5.82; N, 3.87%. Calcd for $C_{14}H_{21}NO_{10}$: C, 46.28; H, 5.82; N, 3.86%.

3-(Aminomethyl)-1,2-O-isopropylidene-α-D-glucofuranose (8). A suspension of **6** (300 mg, 1.07 mmol) and palladium-charcoal (5%, 0.2 g) in water (20 ml) was hydrogenated under hydrogen atmosphere, filtered, and then the filtrate was evaporated. The ninhydrin-positive residue was crystallized from ethanol–ether. Yield, 168 mg (68.2%), mp 122—123 °C, $[\alpha]_D^{23}$ +41.5° (*c* 0.68, EtOH).

Found: C, 47.78; H, 7.68; N, 5.34%. Calcd for $C_{10}H_{19}NO_6$: C, 48.18; H, 7.68; N, 5.62%.

3-(Acetaminomethyl)-5,6-di-O-acetyl-1,2-O-isopropylidene-α-D-glucofuranose (9). To a solution of **8** (100 mg, 0.36 mmol) in pyridine (2 ml) was added acetic anhydride (1 ml), and the mixture was kept at room temperature for 5 h. The solution was treated in the usual procedure to give a sirup which was crystallized from ethanol. Yield, 128 mg (95%), mp 130.5–131 °C; $[\alpha]_D^{23}$ +82.9° (*c* 0.23, $CHCl_3$). IR: 3320 (OH and NH), 1740 (OAc); NMR: 6.40 (NH : t), 5.86 (H_1: d, $J_{1,2}$=3.4), 5.26 (H_5: sex), 4.59 (H_6: q, $J_{5,6}$=2.4), 4.34 (H_2: d), 4.24 ($H_{6'}$: q, $J_{5,6'}$=6.1, $J_{6,6'}$=13.0), 4.06 (H_4: d, $J_{4,5}$=6.4), 3.74 and 3.47 (CH_2: dABq, $J_{A,B}$= 13.0, $J_{NH,3'}$=6.4), 2.12, 2.08, and 2.06 (2×OAc, NAc), 1.51 and 1.32 (2×C-CH_3).

Found: C, 51.16; H, 6.72; N, 3.60%. Calcd for $C_{16}H_{25}NO_9$: C, 51.19; H, 6.71; N, 3.73%.

5,6-Di-O-acetyl-1,2-O-isopropylidene-3-(nitromethyl)-α-D-allofuranose (10). i) From **5**. A solution of **5** (200 mg, 0.6 mmol) in ethanol (5 ml) was added with stirring to a solution of nitromethane (1 ml) and sodium (100 mg, 4.3 mmol) in ethanol (5 ml) at room temperature. After standing the reaction mixture for 30 min, it was neutralized with 60% acetic acid, and then evaporated to give crystals which were recrystallized from ethanol–hexane. Yield, 154 mg (71%), mp 130—132 °C $[\alpha]_D^{23}$ +42.4° (*c* 0.9, $CHCl_3$). IR: 3420 (OH), 1740 (OAc), 1550 (NO_2); NMR: 5.79 (H_1: d, $J_{1,2}$=4.0), 5.22 (H_5: septet), 4.93 and 4.43 (CH_2: ABq, $J_{A,B}$=12.4), 4.77 (H_2: d), 4.40 (H_6: q, $J_{5,6}$=3.5), 4.17 ($H_{6'}$: q, $J_{5,6'}$=6.1, $J_{6,6'}$=12.5), 4.03 (H_4: d, $J_{4,5}$=8.2), 3.30 (OH), 2.10 and 2.06 (2×OAc), 1.58 and 1.37 (2×C-Me).

Found: C, 46.28; H, 5.85; N, 3.80%. Calcd for $C_{14}H_{21}NO_{10}$: C, 46.28; H, 5.83; N, 3.86%.

ii) From 1,2 : 5,6-di-*O*-isopropylidene-3-(nitromethyl)-α-D-allofuranose. A solution of the starting material (500 mg) in acetic acid (70%, 20 ml) was kept at room temperature for 24 h, and then evaporated to give a glassy solid [1,2-*O*-isopropylidene-3-(nitromethyl)-α-D-allofuranose (**11**)] quantitatively, which could not be crystallized. $[\alpha]_D^{23}$ +18.5° (*c*

0.7, MeOH), IR: 1560 (NO_2).

Found: C, 42.55; H, 6.12; N, 4.60%. Calcd for $C_{10}H_{17}NO_8$: C, 43.01; H, 6.14; N, 5.02%.

Acetylation of **11** (200 mg) with acetic anhydride (3 ml) in pyridine (3 ml) in the usual manner gave **10** quantitatively which was identical with the above mentioned sample.

3,5,6-Tri-O-acetyl-3-cyano-1,2-O-isopropylidene-α-D-allofuranose (12). To a solution of **2** (1 g, 4.6 mmol) and hydrogen cyanide (0.3 ml) in pyridine (10 ml) which was stirred at 0 °C for 6 h was added acetic anhydride (3 ml), the mixture was kept at room temperature for 15 h, and the excess hydrogen cyanide was evacuated under reduced pressure. The reaction mixture was poured into ice-water, and the resulting solution was extracted with methylene dichloride. The extracted solution was washed with water and evaporated to give a sirup which was crystallized and recrystallized from ethanol-hexane. Yield, 0.92 g, (54%), mp 140—142 °C, $[\alpha]_D^{23}$ +70.4° (*c* 0.47, $CHCl_3$) [lit,[13] mp 129.5—130.5 °C, $[\alpha]_D^{21}$ +72.8° (*c* 0.3, $CHCl_3$)]. IR and NMR spectra were also identical with those of theauthentic sample.

3-(Hydroxycarbonimidoyl)-1,2-O-isopropylidene-α-D-allofuranose 3',5-Lactone (13). An aqueous solution (2 ml) of potassium cyanide (325 mg, 5 mmol) was added to an aqueous solution (15 ml) of **2** (1.0 g, 4.6 mmol) and sodium hydrogencarbonate (630 mg, 5.1 mmol) with stirring at 0 °C. The crystals deposited immediately were filtered and recrystallized from methanol. Yield, 744 mg (66%), mp 166—168 °C, $[\alpha]_D^{23}$ +60.4° (*c* 0.4, H_2O). IR: 3450 (OH), 3300 (NH), 1705 (-O-C=NH).

Found: C, 48.81; H, 6.07; N, 5.23%. Calcd for $C_{10}H_{15}NO_6$: C, 48.97; H, 6.17; N, 5.71%.

3,6-Di-O-acetyl-3-carboxy-1,2-O-isopropylidene-α-D-allofuranose 3',5-Lactone (14). i) From **13**. To a suspension of **13** (245 mg, 1.0 mmol) in acetic anhydride (1.5 ml) was added pyridine (0.1 ml), and kept at room temperature for 12 h until the mixture became homogenous. The reaction mixture was poured into ice-water to give crystals which were recrystallized from ethanol-hexane. Yield, 201 mg (61%), mp 114—115 °C, $[\alpha]_D^{25}$ +5.2°, $[\alpha]_{365}^{23}$ −28.7° (*c* 0.9, $CHCl_3$), [lit,[14] mp 113—113.5 °C: $[\alpha]_D^{22}$ +6.2°, $[\alpha]_{365}^{23}$ −33.0° (*c* 1.7, $CHCl_3$)].

Found: C, 51.00; H, 5.52%. Calcd for $C_{14}H_{18}O_9$: C, 50.91; H, 5.49%.

IR and NMR spectra were also identical with those of authentic sample.[14]

ii) From **16**. Base-catalyzed acetylation of **16** with acetic anhydride in the usual manner gave **14** quantitatively.

3-[(Acetylimino)methoxymethyl]-3,6-di-O-acetyl-1,2-O-isopropylidene-α-D-allofuranose (15). To a homogeneous reaction mixture of the above experiment was added absolute methanol (4 ml) instead of pouring into ice-water, and then evaporated to give a sirup. The main component of the sirup composed of three components was isolated by TLC (benzene : methanol =8 : 1, and recrystallized form ethanol-hexane. Yield, 273 mg (65%), mp 145—147 °C, $[\alpha]_D^{23}$ +53.5° (*c* 0.6, $CHCl_3$). IR: 3450 (OH), 1765 (OAc), 1660 (C=NAc). NMR: 5.98 (OH : s), 5.85 (H_1 : d, $J_{1,2}$=3.6), 5.34 (H_2 : d), 4.73 (H_4 : d, $J_{4,5}$=1.8), 4.45—4.05 (H_5, H_6, $H_{6'}$: m), 3.30 (OMe), 2.07 and 1.98 (2×OAc, NAc), 1.49 and 1.34 (2×C-CH_3).

Found: C, 50.10; H, 6.19; N, 3.42%. Calcd for $C_{17}H_{25}NO_{10}$: C, 50.61; H, 6.25; N, 3.42%.

3-Carboxy-1,2-O-isopropylidene-α-D-allofuranose Sodium Salt (16). A solution of **13** (245 mg, 1.0 mmol) and sodium hydrogen carbonate (84 mg, 1.0 mmol) in methanol (5 ml) was refluxed for 12 h, evaporated, and the residue was crystallized from ethanol-hexane to give needles quantitatively. Mp 269—271 °C (decomp), $[\alpha]_D^{25}$ +46.6° (*c* 0.9, H_2O). IR: 3350 and 3250 (OH), 1610 (C=O).

Found: C, 41.91; H, 5.42%. Calcd for $C_{10}H_{15}O_8Na$: C, 41.96; H, 5.28%.

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