Syntheses of 6-Deoxyhex-5-enopyranosides from 6-Bromo-6-deoxy- or 6-*O*-*p*-Tolylsulfonylhexopyranosides by the Use of DBU in DMSO

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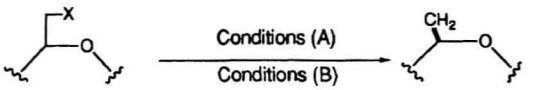
Various kinds of nonbranched and methyl-branched 6-deoxyhex-5-enopyranoside derivatives were prepared from 6-bromo-6-deoxy or 6-*O*-*p*-tolylsulfonylhexopyranoside in a one-pot procedure by a successive treatment with iodide anion and 1,8-diazabicyclo[5.4.0]undec-7-ene in dimethyl sulfoxide. The scope and limitations of this reaction have become apparent by observing the reactions of 18 substrates. The yields of altropyranoside and 2-deoxyribo-hexopyranoside derivatives were high, except for the 2,3-anhydropyranoside derivative. Methyl-branched 6-deoxyhex-5-enopyranoside derivatives were also obtained in practical yields.

6-Deoxyhex-5-enopyranosides are very useful precursors in biologically important natural-product synthesis, such as 6-deoxy-L-hexose[1] and the cyclitol derivative.[2] In general, 6-deoxyhex-5-enopyranosides have been synthesized by treating the corresponding 6-bromo derivative with AgF/pyridine,[3] 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)/CH_3CN[4] or NaH/*N*,*N*-dimethylformamide (DMF).[5] These methods, however, have some limitations, such as displacement reactions with fluorine, acyl migration reaction, and deacylation. At the beginning of our 5-enopyranosides syntheses, we used DBU/CH_3CN as a useful synthetic method; however, it required a longer reaction time and gave side products in many cases. Furthermore, this method did not work well in the case of methyl-branched series. Regarding another type of elimination reaction, S. Hannesian has reported on the use of DBU/DMSO in the synthesis of carbohydrate derivatives containing the vinylic thioether group by eliminating the mesyl group. In that report, the elimination with DBU/DMSO under heating for 2.5 h at 85°C gave the corresponding 2,3-unsaturated derivative in good yield.[6] The strong base ability of DBU/DMSO probably suggests the intermediacy of the DMSO carbo anion in DMSO. If we can use DBU/DMSO methods in the syntheses of hex-5-enopyranosides, the elimination reaction may progress faster than DBU/CH_3CN. In order to contribute to the development of such 6-deoxyhex-5-enopyranosides syntheses, the authors examined DBU/DMSO methods and communicated a convenient and general method for synthesizing 6-deoxyhex-5-enopyranosides from the corresponding 6-bromo-6-deoxy- or 6-*O*-*p*-tolylsulfonylhexopyranosides in a one-pot procedure by a successive treatment with the iodide anion, DBU, and molecular sieves (MS) 4A in dimethyl sulfoxide (DMSO), instead of CH_3CN. This paper describes details concerning the communication[7] as well as the scope and limitations of the above method by using 18 substrates, i.e., nonbranched (**1**, **5**, **8**, **12**, **14**, **16**, **18**, **20**, **22**, **25**, and **28**) and a methyl-branched series (**32**, **34**, **36**, **38**, **40**, **42**, and **44**) (Chart 1, Figs. 1 and 2).

Results and Discussion

Concerning the elimination reaction of the 6-bromo-6-deoxy- or 6-*O*-*p*-tolylsulfonylhexopyranoside derivative, conditions (A): DBU/DMSO, 80—110°C, were selected as preliminary experiments in order to determine the influence of steric factors, functional groups, and protecting groups in this elimination reaction. At first, the gluco series was examined under conditions (A). After methyl 4-*O*-benzoyl-6-bromo-6-deoxy-2,3-di-*O*-methyl-α-D-glucopyranoside (**1**) was treated with 1.2 equiv DBU in DMSO at 110°C (until the starting material disappeared on TLC), the mixture was poured into water and extracted with ethyl acetate to give the desired methyl 4-*O*-benzoyl-6-deoxy-2,3-di-*O*-methyl-α-D-*xylo*-hex-5-enopyranoside (**2**), as well as unexpected by-products methyl 4,6-di-*O*-benzoyl-2,3-di-*O*-methyl-α-D-glucopyranoside (**3**) and methyl 6-*O*-benzoyl-2,3-di-*O*-methyl-α-D-glucopyranoside (**4**) in 32, 28, and 9% yields, respectively. The NMR data of compound **2** showed a disappearance of the H-5 proton and the appearance of methylene protons. Compound **3** showed low-field shifts of the H-6 and H-6′ protons and 10 protons for two benzoyl groups. Compound **4** showed 5 protons for the benzoyl group, a high-field shift of the H-4 proton, and a low-field shift of the H-6 and H-6′ protons. In a similar manner as mentioned above, methyl 4-*O*-benzyl-2,3-di-*O*-methyl-6-*O*-*p*-tolylsulfonyl-α-D-glucopyranoside (**5**) gave the desired methyl 4-*O*-benzyl-6-deoxy-2,3-di-*O*-methyl-α-D-*xylo*-hex-5-enopyranoside (**6**) as well as a 6-hydroxy by-product, methyl 4-*O*-benzyl-2,3-di-*O*-methyl-α-D-glucopyranoside (**7**) in 28 and 38% yields,



Conditions (A): DBU / DMSO, 80-110 °C

Conditions (B): 1) NaI, n-Bu_4NI / DMSO, Molecular sieves 4A
2) DBU / DMSO, 80-120 °C (one-pot)

Chart 1.

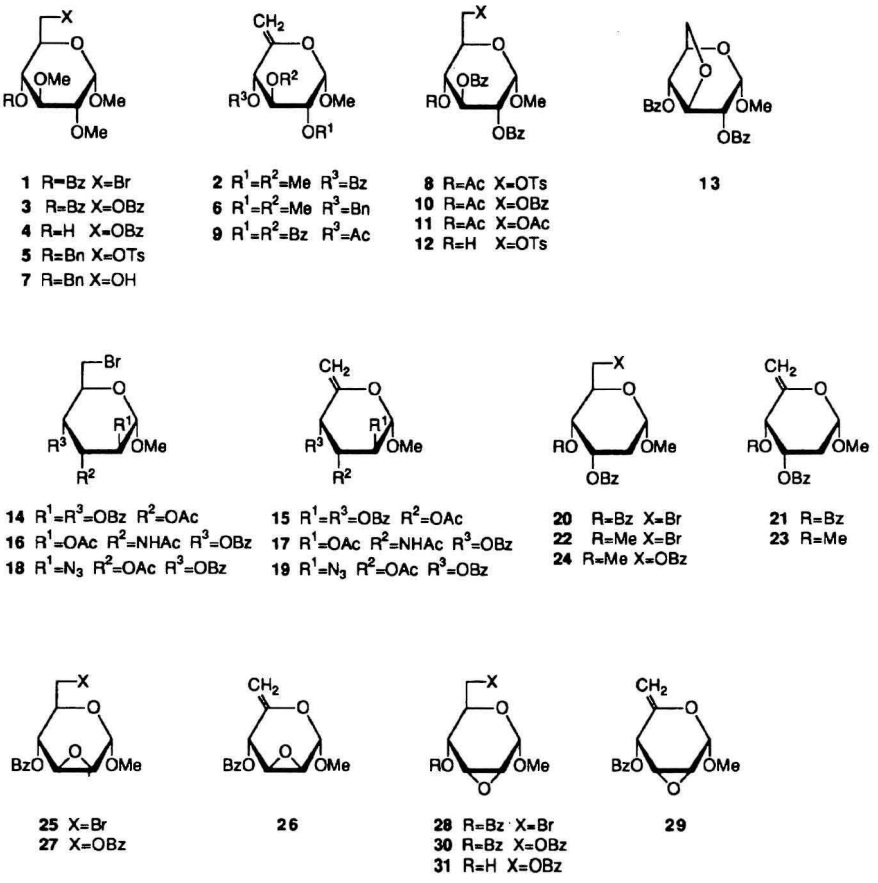


Fig. 1.

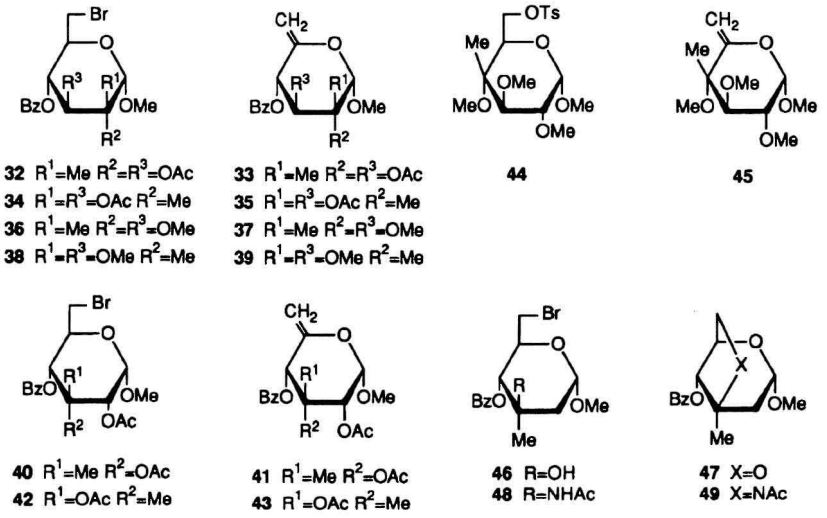


Fig. 2.

respectively. The structure of **7** was supported by a direct comparison with a known compound or the precursor of compound **5**. Under similar conditions, methyl 4-*O*-acetyl-2,3-di-*O*-benzoyl-6-*O*-*p*-tolylsulfonyl-α-D-glucopyranoside (**8**) gave the desired methyl 4-*O*-acetyl-2,3-di-*O*-benzoyl-6-deoxy-α-D-*xylo*-hex-5-enopyranoside (**9**) as well as by-products methyl 4-*O*-acetyl-2,3,6-tri-*O*-benzoyl-α-D-glucopyranoside (**10**) and methyl 4,6-di-*O*-acetyl-2,3-di-*O*-benzoyl-α-D-glucopyranoside (**11**) in 10, 22, and 20% yields, respectively. Compound **10** showed 15 protons for three benzoyl groups and 3 protons for an acetyl group in its NMR data. The other compound

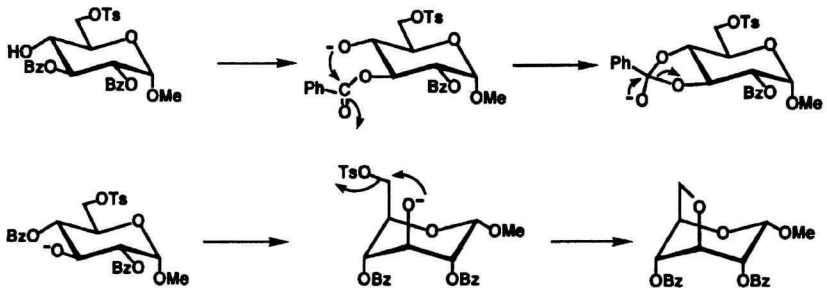
11 showed 10 protons for two benzoyl groups and 6 protons for two acetyl groups. However, it was not easy to determine the structures of compounds **10** and **11**, respectively (especially, the position of the acetyl and benzoyl groups concerned with acyl migration), since the chemical shift of each ring proton is very similar to each other. Therefore, in the determination of the above-mentioned structures compound **10** was directly compared with that obtained by acetylation of methyl 2,3,6-tri-*O*-benzoyl-α-D-glucopyranoside.[8] The structure of compound **11** was determined by a comparison of the physical constants which were derived by acetylation of methyl 2,3-di-*O*-benzoyl-α-D-glucopyranoside. Treatment of methyl 2,3-di-*O*-benzoyl-6-*O*-tolylsulfonyl-α-D-glucopyranoside (**12**) at 80°C for 7.5 h gave the bicyclic compound, methyl 3,6-anhydro-2,4-di-*O*-benzoyl-α-D-glucopyranoside (**13**), in 86% yield. The structure of **13** was supported by IR (no hydroxyl group), the low-field shift of the H-4 proton and the high-field shift of the H-3 proton in the NMR spectrum, indicating benzoyl migration. Furthermore, the conformational change due to the formation of an anhydro ring between C-3 and C-6 was supported by the changed chemical shifts (H-3: ca 1.0 ppm high field shift and H-4: ca 1.0 ppm low field shift) and coupling constants ($J_{1,2}$=3.8 to 3.4 Hz, $J_{2,3}$=9.6 to 4.6 Hz, $J_{3,4}$=9.6 to 5.2 Hz).

Similarly, elimination reactions of altro-, 2-deoxyribo-, and 2,3-anhydro compounds were carried out under conditions (A). In the case of the altro series (**14**, **16**, and **18**), reactions were carried out as follows. Methyl 3-*O*-acetyl-2,4-di-*O*-benzoyl-6-bromo-6-deoxy-α-D-altropyranoside **14**, methyl 3-acetamido-2-*O*-acetyl-4-*O*-benzoyl-6-bromo-3,6-dideoxy-α-D-altropyranoside **16**, and methyl 3-*O*-acetyl-2-azido-4-*O*-benzoyl-6-bromo-2,6-dideoxy-α-D-altropyranoside **18** were treated with DBU in DMSO at 80°C for 2 h to give the corresponding desired 6-deoxyhex-5-enopyranosides, methyl 3-*O*-acetyl-2,4-di-*O*-benzoyl-6-deoxy-α-D-*arabino*-hex-5-enopyranoside (**15**), methyl 3-acetamido-2-*O*-acetyl-4-*O*-benzoyl-3,6-dideoxy-α-D-*arabino*-hex-5-enopyranoside (**17**), and methyl 3-*O*-acetyl-2-azido-4-*O*-benzoyl-2,6-dideoxy-α-D-*arabino*-hex-5-enopyranoside (**19**) in 78, 80, and 82% yields, respectively.

In the case of the 2-deoxyribo series (**20** and **22**), the reactions were carried as follows. Methyl 3,4-di-*O*-benzoyl-6-bromo-2,6-dideoxy-α-D-*ribo*-hexopyranoside **20** was treated at 80°C for 2 h to give the desired methyl 3,4-di-*O*-benzoyl-2,6-dideoxy-α-D-*erythro*-hex-5-enopyranoside (**21**)[3] in 92% yield. In a similar manner as mentioned above, methyl 3-*O*-benzoyl-6-bromo-2,6-dideoxy-4-*O*-methyl-α-D-*ribo*-hexopyranoside (**22**) was treated at a slightly higher temperature (100°C, 3 h) to give the desired methyl 3-*O*-benzoyl-2,6-dideoxy-4-*O*-methyl-α-D-*erythro*-hex-5-enopyranoside (**23**) and a by-product, methyl 3,6-di-*O*-benzoyl-2-deoxy-4-*O*-methyl-α-D-*ribo*-hexopyranoside (**24**), in 54 and 18% yields, respectively. In these ribo series, the yield of the desired hex-5-enopyranoside was affected by the protecting group at the C-4-hydroxyl group (ester or ether). Similar evidence for a decreased yield of the β-elimination product was also observed between the 4-*O*-benzoyl derivative **20** and its 4-*O*-benzyl derivative with AgF/pyridine. The treatment of the compound **20** with AgF/pyridine gave the corresponding hex-5-enopyranoside **21** in 92% yield; a similar treatment of the 4-*O*-benzyl derivative of **20** gave the corresponding hex-5-enopyranoside and 6-fluoro derivative in a ratio of 2:3 in almost quantitative yield.[9] The above results can be explained in terms of the electronic density at C-5, which is induced by the C-4-OH protecting group.

In the case of 2,3-epoxide derivatives (**25** and **28**), reactions were carried out as follows. Methyl 2,3-anhydro-4-*O*-benzoyl-6-bromo-6-deoxy-α-D-mannopyranoside **25** was treated at 80°C for 20 h to give the desired methyl 2,3-anhydro-4-*O*-benzoyl-6-deoxy-α-D-*lyxo*-hex-5-enopyranoside (**26**) as well as an acyl-migrated by-product, methyl 2,3-anhydro-4,6-di-*O*-benzoyl-α-D-mannopyranoside (**27**) in 27 and 16% yields, respectively. In a similar manner to that mentioned above, methyl 2,3-anhydro-4-*O*-benzoyl-6-bromo-6-deoxy-α-D-allopyranoside (**28**) gave the desired methyl 2,3-anhydro-4-*O*-benzoyl-6-deoxy-α-D-*ribo*-hex-5-enopyranoside (**29**) as well as by-products, methyl 2,3-anhydro-4,6-di-*O*-benzoyl-α-D-allopyranoside (**30**) and methyl 2,3-anhydro-6-*O*-benzoyl-α-D-allopyranoside (**31**) in 13, 18, and 7% yields, respectively. The structure of the compound **31** was supported by NMR (5 protons for a benzoyl group and the low field shift of H-6 and H-6′ protons accompanied by a high-field shift of H-4 proton) and IR (ν_{OH} 3490 cm^{-1}) (Fig. 1).

As a result, the yields of the required 6-deoxyhex-5-enopyranosides under conditions (A) were generally low (except for the altro series), and accompanied by side reactions, such as hydroxylation at C-6, acyl migration, and 3,6-anhydro ring formation. The resulting relatively high yields and selective formation of 6-deoxyhex-5-enopyranosides in the altro series (**14** and **16**) can be explained by stereochemically favored conformations of the produced hex-5-enopyranosides, since it is easy to avoid the $A^{1,3}$ strain (between the exo methylene and the benzoyl group at C-4) by a conformational change which could be caused by C-2,3, both axial substituent effects. In this DBU method, the most important factor to reduce the yield of the required 6-deoxyhex-5-enopyranoside seems to be the presence of a free hydroxyl group in the substrate. For example, the presence of a hydroxyl group in compound **12** caused an acyl migration, followed by 3,6-anhydro ring formation by neighboring group participation (stereochemically favored). (Scheme 1) In most cases under conditions (A), acyl migration occurs to give the corresponding 6-*O*-acyl derivatives. These results indicate that one of the reasons for an enhanced yield of the 6-deoxyhex-5-enopyranoside involves hydroxylation at the C-6 position as



Scheme 1.

the first step. In the case of compound **8** (4-*O*-acetyl derivative of **12**), although 3,6-anhydro ring formation is prevented by acetylation of C-4-OH, intermolecular migrations of both the acetyl and benzoyl group occur in preference to 3,6-anhydro ring formation. Judging from the above results, it seem possible to prevent hydroxylation as well as the following acyl migration reactions if the progress of the β-elimination reaction can be controlled under milder conditions. From this point of view, we changed the 6-bromo or 6-*O*-tolylsulfonyl derivatives to the 6-iodo derivative prior to the β-elimination reaction as follows: NaI, *n*-Bu_4NI/DMSO, then DBU/DMSO at 80—110°C (iodonation at C-6 position and elimination in one-pot reaction). In most cases, although some increased yields of 6-deoxyhex-5-enopyranosides were observed, these conditions did not give dramatic results. Finally, we proposed the following practical conditions (B) in order to predominantly obtain the desired β-elimination product. Conditions (B) were carried out in a similar manner as conditions (A), as follows: NaI, *n*-Bu_4NI/DMSO and molecular sieves 4A, then DBU/DMSO at 80—110°C (6-iodonation and elimination in one-pot reaction). Molecular sieves 4A were considered to prevent the hydroxylation reaction at the C-6 position. The optimized conditions for conditions (B) were as follows: A mixture of 6-bromo-6-deoxy or 6-*O*-*p*-tolylsulfonylhexopyranoside, NaI, *n*-Bu_4NI, and molecular sieves 4A in DMSO, was stirred at 80—110°C until the starting hexose disappeared on TLC. After the addition of DBU, the mixture was stirred at 80—110°C until the intermediary 6-iodide derivative disappeared. Under these conditions (B), compounds (**1**, **5**, **8**, **14**, **16**, **18**, **20**, and **22**) were examined in order to compare the yields of hex-5-enopyranoside that were obtained under conditions (A). The yields of hex-5-enopyranosides under conditions (A) were 28—92%, and (B) were 84—95%. (Table 1) Even if under conditions (B), the acyl migration reactions of 2,3-anhydro compounds **25** and **28** could not be prevented. It might be necessary to consider other types of the acyl migration as shown in Scheme 2. Since such compounds as **25** and **28** may have unfavorable steric factors to produce the corresponding hex-5-enopyranosides, it is difficult to avoid the $A^{1,3}$ strain by the rigid bicyclic structure.

In our previous studies concerning the syntheses of branched-chain 6-deoxyhex-5-enopyranosides, both the application of AgF/pyridine and DBU/benzene or toluene to the corresponding 6-bromo derivatives gave unsuccessful results (no reaction). In order to determine the limitation of this method (conditions B), further applications to methyl-branched sugar series (**32**, **34**, **36**, **38**, **40**, **42**, and **44**) were examined (Fig. 2). Under conditions (B), methyl 6-bromo-6-deoxy-α-D-hexopyranosides **32**, **34**, **36**, **38**, **40**, and **42** and 6-*O*-*p*-tolylsulfonyl-α-D-hexopyranoside **44** could also be converted into the corresponding 6-deoxyhex-5-enopyranosides (**33**, **35**, **37**, **39**, **41**, **43**, and **45**) in good yields (Table 2). Judging from the above results, conditions (B) seems to provide a general method for preparing hex-5-enopyranoside in a one-pot reaction. However, it must be noted that the final problems of this reaction are acyl migration and the participation of neighbors. A few instances of neighbor participation, as observed in compound **12**, have also been reported by H. Kodama[10] and M. Matsuzawa,[11] respectively, in the elimination reaction of the compound (**46** and **48**). The elimination reactions of compound **46** with AgF/pyridine at room temperature for 3 h and compound **48** with DBU/benzene under reflux condition for 2 h gave the corresponding bicyclic 3,6-anhydro derivative (**47**)[11] and 3,6-acetylepimino derivative (**49**)[11] in 82 and 83% yields, respectively. In conclusion, it is necessary to consider the steric factor, protecting group, and neighboring participation in order to obtain the corresponding 6-deoxyhex-5-enopyranoside in good yield.

Experimental

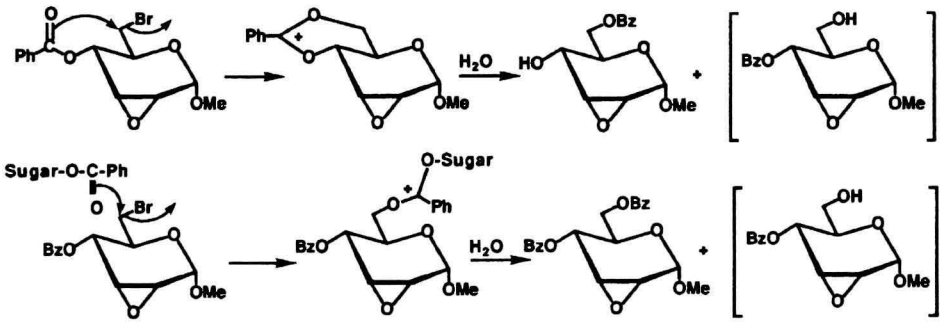
All melting points were uncorrected. The solutions were evaporated under reduced pressure at a bath temperature not exceeding 40°C. The optical rotations were measured in a 0.5 dm tube with a JASCO DIP-140 polarimeter in chloroform. ^1H NMR spectra were recorded in chloroform-*d* with a JEOL FX-200 spectrometer. The chemical shifts, coupling constants, and IR frequencies were recorded in δ, Hz, and cm^{-1} units, respectively.

General Procedures. Conditions (A): A stirring mixture of substrate (0.5 mmol) and 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU, 0.6 mmol) in dry dimethyl sulfoxide (DMSO, 6.0 cm^3) was heated under argon at 80—110°C until the starting compound disappeared on TLC. The reaction mixture was poured into water and extracted with

Table 1. Yields of Hex-5-enopyranosides and By-products under Conditions (A and B)

Substrates	Conditions (A)			Conditions (B)		
	5-Enopyranosides		Others	5-Enopyranosides		Others
1	**2**	32%	**3** 28%, **4** 9%	**2**	85%	
5	**6**	28%	**7** 38%	**6**	88%	
8	**9**	10%	**10** 22%, **11** 20%	**9**	84%	
12	**13**	86%				
14	**15**	78%		**15**	95%	
16	**17**	80%		**17**	84%	
18	**19**	82%		**19**	84%	
20	**21**	92%		**21**	94%	
22	**23**	54%	**24** 18%	**23**	86%	
25	**26**	27%	**27** 16%	**26**	52%	**27** 6%
28	**29**	13%	**30** 18%, **31** 7%	**29**	16%	**30** 20%, **31** 11%

Conditions (A): DBU/DMSO, 80—110°C. Conditions (B): NaI, n-Bu_4NI, MS 4A, DBU/DMSO, 80—110°C.



Scheme 2.

Table 2. Yields of Methyl-Branched Hex-5-enopyranosides under Conditions (B)

Substrates	5-Enopyranosides	
32	**33**	74%
34	**35**	78%
36	**37**	86%
38	**39**	75%
40	**41**	81%
42	**43**	80%
44	**45**	91%

ethyl acetate several times. The combined organic layer was washed with a small amount of water, dried, and evaporated to give products.

Conditions (B): A stirring mixture of the substrate (0.5 mmol), sodium iodide (NaI, 2.5 mmol), tetrabutylammonium iodide (n-Bu_4NI, 0.25 mmol), and molecular sieves 4A (10 pieces) in DMSO (4.0 cm^3) was heated under argon at 80—110°C until the starting compound disappeared on TLC. Then, DBU (0.6 mmol) was added into the reaction mixture, which was kept at 80—110°C (one-pot reaction) until the 6-iodo derivative disappeared. In a similar work up of the reaction mixture, as mentioned in conditions (A), 6-deoxyhex-5-enopyranoside was obtained.

Elimination Reactions of Gluco Series (1, 5, 8, and 12) under the Conditions (A and B). Methyl 4-*O*-Benzoyl-6-deoxy-2,3-di-*O*-methyl-α-D-*xylo*-hex-5-enopyranoside (2), Methyl 4,6-Di-*O*-benzoyl-2,3-di-*O*-methyl-α-D-glucopyranoside (3), and Methyl 6-*O*-Benzoyl-2,3-di-*O*-methyl-α-D-glucopyranoside (4). Conditions (A): A mixture of methyl 4-*O*-benzoyl-6-bromo-6-deoxy-2,3-di-*O*-methyl-α-D-glucopyranoside **1** (200 mg, 0.51 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 94 mg, 0.62 mmol) in dry dimethyl sulfoxide (DMSO, 6.0 cm^3) was heated at 110°C for 3.5 h. The reaction mixture was poured into water and extracted with ethyl acetate several times. The combined organic layer was washed with a small amount of water, dried and evaporated to give a mixture of products. The mixture was purified on preparative TLC (Kieselgel 60, ether–ethyl acetate–hexane=1 : 1 : 2) to give the desired 6-deoxyhex-5-enopyranoside **2**, and by-products 4,6-di-*O*-benzoyl derivative **3** and 6-*O*-benzoyl derivative **4** in 32, 28, and 9% yields, respectively.

2: Mp 109—110°C (ethanol); $[\alpha]_D^{25}$ +122° (c 0.3); IR 1728 (C=O), 1668 (C=C); ^{1}H NMR δ=8.18—8.06 and 7.65—7.44 (5H, m, Ph), 5.58 (1H, ddd, $J_{4,6}$=2.0 Hz, $J_{4,6'}$=2.0 Hz, $J_{4,3}$=9.3 Hz, H-4), 4.96 (1H, d, $J_{1,2}$=3.4 Hz, H-1), 4.72 (1H, dd, $J_{6,6'}$=1.8 Hz, H-6), 4.56 (1H, dd, H-6′), 3.79 (1H, dd, H-3), 3.59, 3.53, and 3.52 (3H×3, each s, OMe×3), 3.49 (1H, dd, $J_{2,3}$=9.3 Hz, H-2). Found: C, 62.08; H, 6.63%. Calcd for $C_{16}H_{20}O_6$: C, 62.32; H, 6.54%.

3: Mp 121—122°C (ethanol); $[\alpha]_D^{25}$ +132° (c 0.7); IR 1725 (C=O); ^{1}H NMR δ=8.10—8.00 and 7.62—7.35 (5H×2, m, Ph×2), 5.32 (1H, dd, $J_{4,5}$=10.0 Hz, H-4), 4.92 (1H, d, $J_{1,2}$=3.4 Hz, H-1), 4.54 (1H, dd, $J_{5,6}$=2.9 Hz, $J_{6,6'}$=12.0 Hz, H-6), 4.35 (1H, dd, $J_{5,6'}$=5.4 Hz, H-6′), 4.16 (1H, ddd, H-5), 3.79 (1H, dd, $J_{3,2}$=9.6 Hz, $J_{3,4}$=9.4 Hz, H-3), 3.57,

3.51, and 3.49 (3H×3, each s, OMe×3), 3.41 (1H, dd, H-2). Found: C, 64.44; H, 6.31%. Calcd for $C_{23}H_{26}O_8$: C, 64.17; H, 6.09%.

4: Mp 68—71°C (ethanol–hexane); $[\alpha]_D^{25}$ +94° (*c* 0.5); IR 3475 (OH), 1722 (C=O); ^{1}H NMR δ=8.08—8.03 and 7.62—7.40 (5H, m, Ph), 4.87 (1H, d, $J_{1,2}$=3.4 Hz, H-1), 4.68 (1H, dd, $J_{5,6}$=4.8 Hz, $J_{6,6'}$=12.2 Hz, H-6), 4.54 (1H, dd, $J_{5,6'}$=2.2 Hz, H-6′), 3.89 (1H, ddd, $J_{5,4}$=9.8 Hz, H-5), 3.66, 3.51, and 3.46 (3H×3, each s, OMe×3), 3.51 (2H, m, H-3 and H-4), 3.25 (1H, dd, $J_{2,3}$=9.5 Hz, H-2), 2.91 (1H, s, OH). Found: C, 58.79; H, 6.59%. Calcd for $C_{16}H_{22}O_7$: C, 58.88; H, 6.80%.

Conditions (B): A mixture of compound **1** (200 mg, 0.51 mmol), sodium iodide (NaI, 385 mg, 2.57 mmol), tetrabutylammonium iodide (Bu_4NI, 94 mg, 0.25 mmol), and molecular sieves 4A (10 pieces) in DMSO (4.0 cm^3) was heated at 80°C for 5 h until the starting compound **1** disappeared on TLC (benzene–acetone=8 : 1). Then, DBU (94 mg, 0.62 mmol) was added to the reaction mixture, which was kept for an additional 6 h at 80°C (one-pot reaction). In a similar work up of the reaction mixture under conditions (A), 6-deoxyhex-5-enopyranoside **2** was obtained in 85% yield.

Methyl 4-*O*-Benzyl-6-deoxy-2,3-di-*O*-methyl-α-D-*xylo*-hex-5-enopyranoside (6) and Methyl 4-*O*-Benzyl-2,3-di-*O*-methyl-α-D-glucopyranoside (7). Conditions (A): A mixture of methyl 4-*O*-benzyl-2,3-di-*O*-methyl-6-*O*-*p*-tolylsulfonyl-α-D-glucopyranoside **5** (218 mg, 0.47 mmol) and DBU (86 mg, 0.57 mmol) in dry DMSO (4.0 cm^3) was heated at 100°C for 7 h. The reaction mixture was worked up in a similar manner as for the reaction of compound **1**; the products were purified on preparative TLC (ethyl acetate–hexane=1 : 2) to give the desired 6-deoxyhex-5-enopyranoside **6** and 6-hydroxy by-product **7**[8] in 28 and 38% yields, respectively.

6: Syrup; $[\alpha]_D^{25}$ +62.0° (*c* 1.2); IR 1665 (C=C); ^{1}H NMR δ=7.42—7.29 (5H, m, Ph), 4.88 (1H, d, $J_{4,6}$=2.0 Hz, $J_{6,6'}$=0 Hz, H-6), 4.87 (1H, d, $J_{1,2}$=3.4 Hz, H-1), 4.78 (2H, s, $-CH_2-$), 4.72 (1H, d, $J_{4,6'}$=2.0 Hz, H-6′), 3.83 (1H, ddd, $J_{4,3}$=8.8 Hz, H-4), 3.64, 3.55, and 3.45 (3H×3, each s, OMe×3), 3.60 (1H, dd, $J_{3,2}$=9.3 Hz, H-3), 3.32 (1H, dd, H-2). Found: C, 64.63; H, 7.64%. Calcd for $C_{16}H_{22}O_5$: C, 65.29; H, 7.53%.

7: Mp 95—96°C (hexane); $[\alpha]_D^{24}$ +162° (*c* 0.8).

Conditions (B): After a mixture of 6-*O*-*p*-tolylsulfonyl derivative **5** (218 mg, 0.47 mmol), NaI (351 mg, 2.34 mmol), Bu_4NI (86 mg, 0.23 mmol), and molecular sieves 4A in DMSO (4.0 cm^3) was stirred under argon at 80°C for 3 h, DBU (86 mg, 0.57 mmol) was added and kept for an additional 3 h at 80°C. A similar work up of the reaction mixture as mentioned above gave **6** in 88% yield.

Methyl 4-*O*-Acetyl-2,3-di-*O*-benzoyl-6-deoxy-α-D-*xylo*-hex-5-enopyranoside (9), Methyl 4-*O*-Acetyl-2,3,6-tri-*O*-benzoyl-α-D-glucopyranoside (10), and Methyl 4,6-Di-*O*-acetyl-2,3-di-*O*-benzoyl-α-D-glucopyranoside (11). Conditions (A): A mixture of methyl 4-*O*-acetyl-2,3-di-*O*-benzoyl-6-*O*-*p*-tolylsulfonyl-α-D-glucopyranoside **8** (218 mg, 0.37 mmol) and DBU (67 mg, 0.44 mmol) in DMSO (4.0 cm^3) was stirred at 100°C for 5 h under argon. The reaction mixture was worked up in a similar manner as mentioned above and the products were purified on preparative TLC (ether–ethyl acetate–hexane =1 : 1 : 2) to give the desired product **9** as well as by-products **10** and **11** in 10, 22, and 20% yields, respectively.

9: Mp 111—112°C (ethanol); $[\alpha]_D^{24}$ +140.5° (*c* 0.4); IR 1731 (C=O) and 1671 (C=C); ^{1}H NMR δ=7.99—7.94 and 7.55—7.33 (5H×2, m, Ph×2), 5.96 (1H, dd, $J_{3,4}$=9.8 Hz, H-3), 5.75 (1H, ddd, $J_{4,6}=J_{4,6'}$=2.0 Hz, H-4), 5.32 (1H, dd, $J_{2,3}$=9.9 Hz, H-2), 5.23 (1H, d, $J_{1,2}$=3.4 Hz, H-1), 4.87 (1H, dd, $J_{6,6'}$=2.0 Hz, H-6), 4.68 (1H, dd, H-6′), 3.48 (3H, s, OMe), 2.06 (3H, s, OAc). Found: C, 64.25; H, 4.98%. Calcd for $C_{23}H_{22}O_8$: C, 64.78; H, 5.20%.

10: Amorphous: $[\alpha]_D^{25}$ +149° (*c* 2.8); IR 1722 (C=O); ^{1}H NMR δ=8.12—7.93 and 7.64—7.33 (5H×3, m, Ph×3), 6.00 (1H, dd, $J_{3,2}$=9.8 Hz, $J_{3,4}$=9.7 Hz, H-3), 5.44 (1H, dd, $J_{4,5}$=9.9 Hz, H-4), 5.23 (1H, dd, $J_{2,1}$=3.4 Hz, H-2), 5.19 (1H, d, H-1), 4.57 (1H, dd, $J_{6,5}$=2.7 Hz, $J_{6,6'}$=12.2 Hz, H-6), 4.46 (1H, dd, $J_{6',5}$=4.9 Hz, H-6′), 4.34 (1H, ddd, H-5), 3.46 (3H, s, OMe), 1.96 (3H, s, OAc). Found: C, 65.17; H, 5.10%. Calcd for $C_{30}H_{28}O_{10}$: C, 65.69; H, 5.15%.

11: Syrup: $[\alpha]_D^{24}$ +141° (*c* 1.6); IR 1734 (C=O); ^{1}H NMR δ=7.99—7.92 and 7.56—7.33 (5H×2, m, Ph×2), 5.96 (1H, dd, $J_{3,4}$=9.8 Hz, $J_{3,2}$=8.1 Hz, H-3), 5.35 (1H, dd, $J_{4,5}$=9.9 Hz, H-4), 5.21 (1H, dd, $J_{2,1}$=3.4 Hz, $J_{2,3}$=8.1 Hz, H-2), 5.19 (1H, d, H-1), 4.35 (1H, dd, $J_{6,5}$=4.6 Hz, $J_{6,6'}$=12.3 Hz, H-6), 4.18 (1H, dd, $J_{6',5}$=2.2 Hz, H-6′), 4.14 (1H, ddd, H-5), 3.45 (3H, s, OMe), 2.15 and 1.96 (3H×2, each s, OAc×2). Found: C, 62.21; H, 5.50%. Calcd for $C_{25}H_{26}O_{10}$: C, 61.72; H, 5.35%.

Conditions (B): After a mixture of compound **8** (218 mg, 0.37 mmol), NaI (273 mg, 1.82 mmol), Bu_4NI (68 mg, 0.18 mmol), and molecular sieves 4A (10 pieces) in DMSO (4.0 cm^3) was stirred for 6 h at 80°C under argon, DBU (67 mg, 0.44 mmol) was added and kept for an additional 3 h at 80°C. A similar work up of the reaction mixture as mentioned above gave **9** in 84% yield.

Methyl 3,6-Anhydro-2,4-di-*O*-benzoyl-α-D-glucopyranoside (13). Conditions (A): A mixture of methyl 2,3-di-*O*-benzoyl-6-*O*-*p*-tolylsulfonyl-α-D-glucopyranoside **12** (200 mg, 0.36 mmol) and DBU (65 mg, 0.43 mmol) in DMSO (6.0 cm^3) was heated at 80°C for 3 h; the usual work up of the reaction mixture and purification gave the 3,6-anhydro derivative **13** in 86% yield.

13: Syrup; $[\alpha]_D^{25}$ +19.3° (*c* 0.7); IR 1725 (C=O); ^{1}H NMR δ=8.06—7.79 and 7.58—7.01 (5H×2, m, Ph×2), 5.37 (1H, dd, $J_{2,1}$=3.4 Hz, $J_{2,3}$=4.6 Hz, H-2), 5.18 (1H, d, H-1), 5.03 (1H, dd, $J_{4,3}$=5.2 Hz, $J_{4,5}$=2.6 Hz, H-4), 4.87 (1H, dd, H-3), 4.75 (1H, dd, $J_{5,6}$=0 Hz, $J_{5,6'}$=2.9 Hz, H-5), 4.33 (1H, d, $J_{6,6'}$=10.7 Hz, H-6), 4.12 (1H, dd, H-6′). Found: C, 66.01; H, 5.59%. Calcd for $C_{21}H_{20}O_7$; C, 65.61; H, 5.24%.

Elimination Reactions of Altro Series (14, 16, and 18) under Conditions (A and B). Methyl 3-*O*-Acetyl-2,4-di-*O*-benzoyl-6-deoxy-α-D-*arabino*-hex-5-enopyranoside (15). Conditions (A): A mixture of methyl 3-*O*-acetyl-2,4-di-*O*-benzoyl-6-bromo-6-deoxy-α-D-altropyranoside **14** (203 mg, 0.40 mmol) and DBU (74 mg, 0.49 mmol) in DMSO (4.0 cm^3) was heated at 80°C for 2 h under argon. The reaction mixture was worked up in a similar manner to that mentioned above. The product was purified on preparative TLC (ether–ethyl acetate–hexane =1 : 1 : 2) to give the corresponding 6-deoxyhex-5-enopyranoside derivative **15** in 78% yield.

15: Syrup; $[\alpha]_D^{25}$ −38° (*c* 1.0); IR 1731 (C=O), 1668 (C=C); ^{1}H NMR δ=8.13—8.03 and 7.64—7.43 (5H×2, m, Ph×2), 6.03 (1H, d, $J_{4,3}$=3.7 Hz, H-4), 5.67 (1H, dd, $J_{2,1}$=

5.4 Hz, $J_{2,3}$=8.8 Hz, H-2), 5.42 (1H, dd, H-3), 4.97 (1H, d, $J_{6,6'}$=1.2 Hz, H-6), 4.88 (1H, d, H-6'), 4.80 (1H, d, H-1), 3.58 (3H, s, OMe), 1.96 (3H, s, OAc). Found: C, 65.02; H, 5.23%. Calcd for $C_{23}H_{22}O_8$: C, 64.78; H, 5.20%.

Conditions (B): After a mixture of compound **14** (203 mg, 0.40 mmol), NaI (304 mg, 2.03 mmol), Bu_4NI (75 mg, 0.20 mmol), and molecular sieves 4A (10 pieces) in DMSO (4.0 cm^3) was treated at 80°C for 3 h under argon, DBU (74 mg, 0.49 mmol) was added and kept for 1.5 h at 80°C. A similar work up of the reaction mixture as mentioned above gave **15** in 95% yield.

Methyl 3-Acetamido-2-*O*-acetyl-4-*O*-benzoyl-3,6-dideoxy-α-D-*arabino*-hex-5-enopyranoside (17). Conditions (A): A mixture of methyl 3-acetamido-2-*O*-acetyl-4-*O*-benzoyl-6-bromo-3,6-dideoxy-α-D-altropyranoside **16** (201 mg, 0.45 mmol) and DBU (82 mg, 0.54 mmol) in DMSO (5.0 cm^3) was stirred at 80°C for 2 h under argon; usual work up of the reaction mixture and purification on preparative TLC gave **17** in 80% yield.

17: Syrup; $[\alpha]_D^{24}$ −14.4° (*c* 0.6); IR 3430 (N–H), 1728 (C=O), 1668 (HN–C=O, C=C); ^{1}H NMR δ=8.05—8.00 and 7.62—7.40 (5H, m, Ph), 6.35 (1H, d, $J_{NH,3}$=9.8 Hz, NH), 5.84 (1H, d, $J_{4,3}$=4.4 Hz, H-4), 5.02 (1H, dd, $J_{2,1}$=2.9 Hz, $J_{2,3}$=5.4 Hz, H-2), 4.91 (1H, s, H-6), 4.81 (1H, s, H-6'), 4.77 (1H, d, H-1), 4.76 (1H, ddd, H-3), 3.55 (3H, s, OMe), 2.15 (3H, s, OAc), 1.95 (3H, s, NAc). Found: C, 59.63; H, 5.57; N, 3.61%. Calcd for $C_{18}H_{21}NO_7$: C, 59.49; H, 5.83; N, 3.86%.

Conditions (B): After a mixture of the compound **16** (201 mg, 0.45 mmol), NaI (340 mg, 2.27 mmol), Bu_4NI (84 mg, 0.23 mmol), and molecular sieves 4A (10 pieces) in DMSO (4.0 cm^3) was stirred for 4 h at 80°C under argon, DBU (83 mg, 0.55 mmol) was added and kept for an additional 1.5 h at 80°C. A similar work up of the reaction mixture and purification gave **17** in 84% yield.

Methyl 3-*O*-Acetyl-2-azido-4-*O*-benzoyl-2,6-dideoxy-α-D-*arabino*-hex-5-enopyranoside (19). Conditions (A): A mixture of methyl 3-*O*-acetyl-2-azido-4-*O*-benzoyl-6-bromo-2,6-dideoxy-α-D-altropyranoside **18** (102 mg, 0.24 mmol) and DBU (45 mg, 0.30 mmol) in DMSO (1.5 cm^3) was stirred for 2 h at 80°C under argon. The reaction mixture was worked up in the usual manner to give syrupy **19**, which was purified on a column of silica gel (hexane–ethyl acetate=2 : 1) in 82% yield.

19: Syrup: $[\alpha]_D^{25}$ +18.1° (*c* 0.5); IR 2116 (N_3), 1758 and 1728 (C=O), 1668 (C=C); ^{1}H NMR δ=8.09—7.43 (5H, m, Ph), 5.88 (1H, d, $J_{4,3}$=3.4, H-4), 4.95 (1H, d, $J_{6,6'}$=1.5, H-6), 4.94 (1H, dd, H-3), 4.87 (1H, d, H-6'), 4.42 (1H, d, $J_{1,2}$=7.6 Hz, H-1), 3.98 (1H, dd, $J_{2,3}$=10.8 Hz, H-2), 3.68 (3H, s, OMe), 2.05 (3H, s, OAc). Found: C, 55.12; H, 4.78; N, 11.70%. Calcd for $C_{16}H_{17}N_3O_6$: C, 55.33; H, 4.93; N, 12.10%.

Conditions (B): After a mixture of the compound **18** (216 mg, 0.50 mmol), NaI (378 mg, 2.52 mmol), and Bu_4NI (93 mg, 0.25 mmol) in DMSO (5.0 cm^3) was stirred for 3 h at 80°C under argon, DBU (93 mg, 0.61 mmol) and molecular sieves 4A (10 pieces) were added and kept for an additional 1.5 h at 80°C. A similar work up of the reaction mixture as mentioned above gave **19** in 84% yield.

Elimination Reactions of 2-Deoxyribo Series (20 and 22) under Conditions (A and B). Methyl 3,4-Di-*O*-Benzoyl-2,6-dideoxy-α-D-*erythro*-hex-5-enopyranoside (21). Conditions (A): A mixture of methyl 3,4-di-*O*-benzoyl-6-bromo-2,6-dideoxy-α-D-*ribo*-hexopyranoside **20** (266 mg, 0.59 mmol) and DBU (108 mg, 0.71 mmol) in DMSO (4.0 cm^3) was stirred for 2 h at 80°C under argon. The reaction mixture was purified on preparative TLC (CCl_4–ether=5 : 2) to give the corresponding product **21** in 92% yield.

21: Syrup; $[\alpha]_D^{25}$ +122° (*c* 1.0); IR 1725 (C=O), 1665 (C=C); ^{1}H NMR δ=8.06—7.95 and 7.60—7.34 (5H×2, m, Ph×2), 5.87 (1H, d, $J_{4,3}$=3.2 Hz, H-4), 5.48 (1H, ddd, $J_{3,2a}$=8.1 Hz, $J_{3,2e}$=4.8 Hz, H-3), 4.90 (1H, d, $J_{6,6'}$=1.0 Hz, H-6), 4.83 (1H, dd, $J_{1,2a}$=5.7 Hz, $J_{1,2e}$=3.9 Hz, H-1), 4.82 (1H, d, H-6'), 3.58 (3H, s, OMe), 2.43 (1H, ddd, $J_{2a,2e}$=13.6 Hz, H-2a), 2.35 (1H, ddd, H-2e). Found: C, 68.21; H, 5.44%. Calcd for $C_{21}H_{20}O_6$; C, 68.47; H, 5.47%. [Ref. 3: $[\alpha]_D^{23}$ +123° (*c* 2.9); IR 1730 (C=O), 1660 (C=C); ^{1}H NMR: in benzene-d_6 δ=8.14—8.00 and 7.20—6.86 (5H×2, m, Ph×2), 5.96 (1H, d, $J_{4,3}$=3.2 Hz, H-4), 5.37 (1H, ddd, $J_{3,2a}$=8.9 Hz, $J_{3,2e}$=4.2 Hz, H-3), 4.75 (1H, d, $J_{6,6'}$=1.0 Hz, H-6), 4.65 (1H, d, H-6'), 4.33 (1H, dd, $J_{1,2a}$=6.2 Hz, $J_{1,2e}$=3.5 Hz, H-1), 3.25 (3H, s, OMe), 2.32 (1H, ddd, $J_{2a,2e}$=13.5 Hz, H-2a), 1.92 (1H, ddd, H-2e)].

Conditions (B): After a mixture of the compound **20** (266 mg, 0.59 mmol), NaI (534 mg, 3.56 mmol), and Bu_4NI (109 mg, 0.30 mmol) in DMSO (4.0 cm^3) was stirred for 3 h at 80°C under argon until the disappearance of **20** (TLC: CCl_4–ether=5 : 2), DBU (108 mg, 0.71 mmol) and molecular sieves 4A (10 pieces) were added and kept for an additional 1.5 h at 80°C. A similar work up of the reaction mixture, the purification of the product on TLC (as mentioned above) gave product **21** in 94% yield.

Methyl 3-*O*-Benzoyl-2,6-dideoxy-4-*O*-methyl-α-D-*erythro*-hex-5-enopyranoside (23) and Methyl 3,6-di-*O*-benzoyl-2-deoxy-4-*O*-methyl-α-D-*ribo*-hexopyranoside (24). Conditions (A): A mixture of methyl 3-*O*-benzoyl-6-bromo-2,6-dideoxy-4-*O*-methyl-α-D-*ribo*-hexopyranoside (**22**) (180 mg, 0.50 mmol) and DBU (92 mg, 0.61 mmol) in DMSO (5.0 cm^3) was stirred at 100°C for 3 h. The products were extracted with ethyl acetate and purified on TLC (ether–hexane=1 : 1) to give the desired compound **23** and by-product **24** in 54 and 18% yields, respectively.

23: Syrup; $[\alpha]_D^{24}$ +116° (*c* 1.3); IR 1728 (C=O), 1668 (C=C); ^{1}H NMR δ=8.18—8.05 and 7.61—7.40 (5H, m, Ph), 5.26 (1H, ddd, $J_{3,4}$=3.2 Hz, $J_{3,2a}$=10.0 Hz, $J_{3,2e}$=3.2 Hz, H-3), 4.87 (1H, s, H-6), 4.69 (1H, dd, $J_{1,2a}$=7.4 Hz, $J_{1,2e}$=3.2 Hz, H-1), 4.66 (1H, s, H-6'), 3.94 (1H, d, H-4), 3.55 and 3.38 (3H×2, each s, OMe×2), 2.38 (1H, ddd, $J_{2a,2e}$=13.1 Hz, H-2a), 2.14 (1H, ddd, H-2e). Found: C, 64.91; H, 6.61%. Calcd for $C_{15}H_{18}O_5$: C, 64.73; H, 6.52%.

24: Syrup; $[\alpha]_D^{24}$ +113° (*c* 0.8); IR 1725 (C=O); ^{1}H NMR δ=8.14—8.07 and 7.62—7.42 (5H×2, m, Ph×2), 5.77 (1H, ddd, $J_{3,4}$=3.2 Hz, $J_{3,2e}$=3.2 Hz, $J_{3,2a}$=3.2 Hz, H-3), 4.82 (1H, d, $J_{1,2a}$=4.2 Hz, $J_{1,2e}$=0 Hz, H-1), 4.67 (1H, dd, $J_{6,5}$=2.2 Hz, $J_{6,6'}$=11.5 Hz, H-6), 4.56 (1H, dd, $J_{6',5}$=5.4 Hz, H-6'), 4.45 (1H, ddd, $J_{5,4}$=9.9 Hz, H-5), 3.47 (1H, dd, H-4), 3.43 and 3.39 (3H×2, each s, OMe×2), 2.30 (1H, dd, $J_{2a,2e}$=15.2 Hz, H-2e), 2.06 (1H, ddd, H-2a). Found: C, 65.88; H, 5.93%. Calcd for $C_{22}H_{24}O_7$: C, 65.99; H, 6.04%.

Conditions (B): After a mixture of 6-bromo-derivative **22** (180 mg, 0.50 mmol), NaI (451 mg, 3.01 mmol), and Bu_4NI (93 mg, 0.25 mmol) in DMSO (5.0 cm^3) was stirred at 80°C for 4 h until the disappearance of the starting com-

pound **22**, DBU (92 mg, 0.61 mmol) and molecular sieves 4A (10 pieces) were added and kept for an additional 3 h. The reaction mixture was worked up in a similar manner as conditions (A) to give **23** in 86% yield.

Elimination Reactions of 2,3-Anhydro Series (25 and 28) under the Conditions (A and B). Methyl 2,3-Anhydro-4-*O*-benzoyl-α-D-*lyxo*-hex-5-enopyranoside (26) and Methyl 2,3-Anhydro-4,6-di-*O*-benzoyl-α-D-mannopyranoside (27). Conditions (A): A mixture of methyl 2,3-anhydro-4-*O*-benzoyl-6-bromo-6-deoxy-α-D-mannopyranoside (**25**) (500 mg, 1.45 mmol) and DBU (266 mg, 1.75 mmol) in dry DMSO (11.5 cm^3) was stirred at 80°C for 20 h. The reaction mixture was poured into brine and extracted with ethyl acetate several times. The usual work up of the products and purification on a column of silica gel (Wakogel C-300, hexane–ethyl acetate=6 : 1) gave the corresponding hexosene derivative **26** and 4,6-di-*O*-benzoyl derivative **27** in 27 and 16% yields, respectively.

26: Syrup; $[\alpha]_D^{25}$ +16.2° (*c* 0.9); IR 1725 (C=O), 1659 (C=C); ^{1}H NMR δ=8.13—7.35 (5H, m, Ph), 5.95 (1H, d, $J_{4,3}$=1.7 Hz, H-4), 5.17 (1H, d, $J_{1,2}$=1.4 Hz, H-1), 4.72 (1H, d, $J_{6,6'}$=1.4 Hz, H-6), 4.58 (1H, d, H-6′), 3.61 (3H, s, OMe), 3.50 (1H, dd, $J_{3,2}$=3.8 Hz, $J_{3,4}$=1.7 Hz, H-3), 3.33 (1H, dd, H-2). Found: C, 63.72; H, 5.32%. Calcd for $C_{14}H_{14}O_5$: C, 64.11; H, 5.38%.

27: Syrup; $[\alpha]_D^{25}$ +119.7° (*c* 0.7); IR 1722 (C=O); ^{1}H NMR δ=8.08—7.35 (5H×2, m, Ph×2), 5.23 (1H, d, $J_{4,5}$=9.8 Hz, $J_{4,3}$=0 Hz, H-4), 5.00 (1H, s, $J_{1,2}$=0 Hz, H-1), 4.52 (1H, dd, $J_{6,5}$=2.9 Hz, $J_{6,6'}$=11.7 Hz, H-6), 4.37 (1H, dd, $J_{6',5}$=6.1 Hz, H-6′), 4.22 (1H, ddd, H-5), 3.52 (3H, s, OMe), 3.40 (1H, d, $J_{3,2}$=3.4 Hz, H-3), 3.17 (1H, d, H-2). Found: C, 65.35; H, 5.18%. Calcd for $C_{21}H_{20}O_7$: C, 65.61; H, 5.24%.

Conditions (B): After a mixture of 6-bromo derivative **25** (200 mg, 0.58 mmol), NaI (473 mg, 3.16 mmol), Bu_4NI (108 mg, 0.29 mmol), and molecular sieves 4A (10 pieces) in dry DMSO (4.0 cm^3) was stirred at 80°C for 4 h, DBU (106 mg, 0.70 mmol) was added and stirred for an additional 3.5 h at 80°C. The reaction mixture was worked up in a similar manner as mentioned above to give the desired product **26** and by-product **27** in 52 and 6% yields, respectively.

Methyl 2,3-Anhydro-4-*O*-benzoyl-α-D-*ribo*-hex-5-enopyranoside (29), Methyl 2,3-Anhydro-4,6-di-*O*-benzoyl-α-D-allopyranoside (30), and Methyl 2,3-Anhydro-6-*O*-benzoyl-α-D-allopyranoside (31). Conditions (A): A mixture of methyl 2,3-anhydro-4-*O*-benzoyl-6-bromo-6-deoxy-α-D-allopyranoside **28** (204 mg, 0.59 mmol) and DBU (108 mg, 0.71 mmol) in DMSO (4.7 cm^3) was stirred at 80°C for 24 h under argon. A similar work up of the reaction mixture as mentioned above, and then purification on a column of silica gel (hexane–ethyl acetate=2 : 1), gave a mixture of hexosene **29**, 4,6-di-*O*-benzoyl derivative **30**, and 6-*O*-benzoyl derivative **31**, which were separated by recrystallization (ethanol–hexane) and on a column of silica gel. The yields of products **29**, **30**, and **31** were 13, 18, and 7%, respectively.

29: Syrup; $[\alpha]_D^{25}$ +255.1° (*c* 1.0); IR 1725 (C=O), 1665 (C=C); ^{1}H NMR δ=8.17—7.34 (5H, m, Ph), 5.93 (1H, ddd, $J_{4,3}$=1.7 Hz, $J_{4,6}$=2.0 Hz, $J_{4,6'}$=2.0 Hz, H-4), 5.10 (1H, d, $J_{1,2}$=2.4 Hz, H-1), 4.85 (1H, dd, $J_{6,6'}$=1.7 Hz, H-6), 4.77 (1H, dd, H-6′), 3.63 (1H, dd, $J_{3,2}$=3.4 Hz, H-3), 3.60 (1H, dd, H-2), 3.59 (3H, s, OMe). Found: C, 64.04; H, 5.37%. Calcd for $C_{14}H_{14}O_5$: C, 64.12; H, 5.38%.

30: Mp 123—124°C (ethanol–hexane); $[\alpha]_D^{25}$ +177.2° (*c* 0.7); IR 1722 (C=O); ^{1}H NMR δ=8.08—7.38 (5H×2, m, Ph×2), 5.45 (1H, dd, $J_{4,3}$=1.7 Hz, $J_{4,5}$=9.5 Hz, H-4), 5.00 (1H, d, $J_{1,2}$=3.2 Hz, H-1), 4.56 (1H, dd, $J_{6,5}$=4.4 Hz, $J_{6,6'}$= 13.7 Hz, H-6), 4.42 (1H, ddd, $J_{5,6'}$=1.7 Hz, H-5), 4.39 (1H, dd, H-6′), 3.73 (1H, dd, $J_{3,2}$=4.2 Hz, H-3), 3.62 (1H, dd, H-2), 3.51 (3H, s, OMe). Found: C, 65.18; H, 5.27%. Calcd for $C_{21}H_{20}O_7$: C, 65.62; H, 5.24%.

31: Mp 142—143°C (ethanol–hexane); $[\alpha]_D^{25}$ +114.6° (*c* 0.3); IR 3490 (OH), 1698 (C=O); ^{1}H NMR δ=8.08—7.36 (5H, m, Ph), 4.92 (1H, d, $J_{1,2}$=3.2 Hz, H-1), 4.63 (1H, dd, $J_{6,5}$=4.6 Hz, $J_{6,6'}$=12.2 Hz, H-6), 4.54 (1H, dd, $J_{6',5}$=2.3 Hz, H-6′), 3.96 (1H, ddd, $J_{5,4}$=4.3 Hz, H-5), 3.94 (1H, dd, $J_{4,3}$=2.3 Hz, H-4), 3.58 (1H, dd, $J_{2,3}$=4.2 Hz, H-2), 3.52 (1H, dd, H-3), 3.46 (3H, s, OMe), 2.62 (1H, bs, OH). Found: C, 59.64; H, 5.90%. Calcd for $C_{14}H_{16}O_6$: C, 59.99; H, 5.75%.

Conditions (B): After a mixture of 6-bromo derivative **28** (234 mg, 0.68 mmol), NaI (511 mg, 3.41 mmol), Bu_4NI (126 mg, 0.34 mmol), and molecular sieves 4A (10 pieces) in DMSO (4.7 cm^3) was stirred at 80°C for 3.5 h under argon, DBU (125 mg, 0.82 mmol) was added and stirred for an additional 16 h. A similar work up of the reaction mixture as conditions (A) gave the corresponding products **29**, **30**, and **31** in 16, 20, and 11% yields, respectively.

Elimination Reactions of Methyl-Branched Hexopyranoside Series (32, 34, 36, 38, 40, 42, and 44) under the Conditions (B). Methyl 2,3-Di-*O*-acetyl-4-*O*-benzoyl-2-*C*-methyl-α-D-*xylo*-hex-5-enopyranoside (33). After a mixture of methyl 2,3-di-*O*-acetyl-4-*O*-benzoyl-6-bromo-6-deoxy-2-*C*-methyl-α-D-glucopyranoside **32** (500 mg, 1.09 mmol), NaI (950 mg, 6.34 mmol), and Bu_4NI (230 mg, 0.62 mmol) in DMSO (50 cm^3) was stirred under argon in the presence of molecular sieves 4A (20 pieces) at 80°C for 8 h, DBU (970 mg, 6.38 mmol) was added and kept until the disappearance of the 6-iodo derivative (for 12 h). The reaction mixture was purified directly on a column of silica gel (Kieselgel 60, ethanol–hexane=1 : 2) and recrystallized to give the corresponding enopyranoside **33** in 74% yield.

33: Mp 106—107°C (ethanol–hexane); $[\alpha]_D^{25}$ +53.0° (*c* 0.2); IR 1770 and 1750 (C=O), 1680 (C=C); ^{1}H NMR δ= 8.10—7.43 (5H, m, Ph), 5.72 (1H, d, $J_{3,4}$=10.2 Hz, H-3), 5.64 (1H, ddd, $J_{4,6}$=$J_{4,6'}$=2.0 Hz, H-4), 5.59 (1H, s, H-1), 4.77 (1H, dd, $J_{6,6'}$=2.0 Hz, H-6), 4.58 (1H, dd, H-6′), 3.45 (3H, s, OMe), 2.01 and 1.98 (3H×2, each s, OAc×2), 1.72 (3H, s, C-Me). Found: C, 60.03; H, 5.65%. Calcd for $C_{19}H_{22}O_8$: C, 60.31; H, 5.86%.

Methyl 2,3-Di-*O*-acetyl-4-*O*-benzoyl-2-*C*-methyl-α-D-*lyxo*-hex-5-enopyranoside (35). Methyl 2,3-di-*O*-acetyl-4-*O*-benzoyl-6-bromo-6-deoxy-2-*C*-methyl-α-D-mannopyranoside **34** was treated in a similar manner as mentioned above to give the corresponding enopyranoside **35** in 78% yield.

35: Syrup; $[\alpha]_D^{23}$ −20.3° (*c* 0.2); IR 1760 and 1740 (C=O), 1670 (C=C); ^{1}H NMR δ=8.09—7.36 (5H, m, Ph), 5.97 (1H, ddd, $J_{4,3}$=10.0 Hz, $J_{4,6}$=$J_{4,6'}$=2.0 Hz, H-4), 5.58 (1H, d, H-3), 5.57 (1H, s, H-1), 4.77 (1H, dd, $J_{6,6'}$=1.7 Hz, H-6), 4.54 (1H, dd, H-6′), 3.49 (3H, s, OMe), 2.14 and 1.99 (3H×2, each s, OAc×2), 1.56 (3H, s, C-Me). Found: C, 59.92; H, 5.73%. Calcd for $C_{19}H_{22}O_8$: C, 60.31; H, 5.86%.

Methyl 4-*O*-Benzoyl-2,3-di-*O*-methyl-2-*C*-methyl-α-D-*xylo*-hex-5-enopyranoside (37). After a mixture of methyl 4-*O*-benzoyl-6-bromo-6-deoxy-2,3-di-*O*-methyl-2-*C*-methyl-α-D-glucopyranoside **36** (500 mg, 1.24 mmol), NaI (1.12 g, 7.47 mmol), and Bu_4NI (275 mg, 0.74 mmol) in DMSO (80 cm^3) was stirred under argon in the presence of molecular sieves 4A (20 pieces) at 80°C for 8 h, DBU (905 mg, 5.95 mmol) was added and kept at 80°C until the disappearance of the 6-iodo derivative (for 14 h). A similar work up of the reaction mixture as mentioned above gave **37** in 86% yield.

37: Mp 99—101°C (ethanol–hexane); $[\alpha]_D^{25}$ +53.0° (*c* 0.2); IR 1729 (C=O), 1680 (C=C); ^{1}H NMR δ=8.13—7.44 (5H, m, Ph), 5.62 (1H, ddd, $J_{4,3}$=9.5 Hz, $J_{4,6}$=$J_{4,6'}$=2.2 Hz, H-4), 4.70 (1H, dd, $J_{6,6'}$=2.2 Hz, H-6), 4.67 (1H, s, H-1), 4.50 (1H, dd, H-6′), 3.82 (1H, d, H-3), 3.51 3.50, and 3.38 (3H×3, each s, OMe×3), 1.42 (3H, s, C-Me). Found: C, 63.49; H, 7.03%. Calcd for $C_{17}H_{22}O_6$: C, 63.34; H, 6.88%.

Methyl 4-*O*-Benzoyl-2,3-di-*O*-methyl-2-*C*-methyl-α-D-*lyxo*-hex-5-enopyranoside (39). Methyl 4-*O*-benzoyl-6-bromo-6-deoxy-2,3-di-*O*-methyl-2-*C*-methyl-α-D-mannopyranoside **38** was treated in a similar manner as mentioned above to give the corresponding enopyranoside **39** in 75% yield.

39: Syrup; IR 1730 (C=O), 1680 (C=C); ^{1}H NMR δ=8.17—7.41 (5H, m, Ph), 6.03 (1H, ddd, $J_{4,3}$=10.0 Hz, $J_{4,6}$=$J_{4,6'}$=2.2 Hz, H-4), 4.67 (1H, dd, $J_{6,6'}$=2.2 Hz, H-6), 4.67 (1H, s, H-1), 4.46 (1H, dd, H-6′), 3.61 (1H, d, H-3), 3.50, 3.47, and 3.42 (3H×3, each s, OMe×3), 1.37 (3H, s, CMe). Found: C, 63.52; H, 7.05%. Calcd for $C_{17}H_{22}O_6$: C, 63.34; H, 6.88%.

Methyl 2,3-Di-*O*-acetyl-4-*O*-benzoyl-3-*C*-methyl-α-D-*ribo*-hex-5-enopyranoside (41). Methyl 2,3-di-*O*-acetyl-4-*O*-benzoyl-6-bromo-6-deoxy-3-*C*-methyl-α-D-allopyranoside **40** was treated in a similar manner as in the case of compound **33** to give the corresponding enopyranoside **41** in 81% yield.

41: Syrup; $[\alpha]_D^{23}$ +50.2° (*c* 1.0); IR 1760 and 1740 (C=O), 1675 (C=C); ^{1}H NMR δ=8.31—7.17 (5H, m, Ph), 5.95 (1H, s, H-4), 5.51 (1H, d, $J_{2,1}$=2.4 Hz, H-2), 5.00 (1H, s, H-6), 4.97 (1H, s, H-6′), 4.81 (1H, d, H-1), 3.62 (3H, s, OMe), 2.28 and 1.93 (3H×2, each s, OAc×2), 1.77 (3H, s, C-Me). Found: C, 60.04; H, 5.98%. Calcd for $C_{19}H_{22}O_8$: C, 60.31; H, 5.86%.

Methyl 2,3-Di-*O*-acetyl-4-*O*-benzoyl-α-D-*xylo*-hex-5-enopyranoside (43). Methyl 2,3-di-*O*-acetyl-4-*O*-benzoyl-6-bromo-6-deoxy-3-*C*-methyl-α-D-glucopyranoside **42** was treated in a similar manner as in the case of compound **32** to give the corresponding enopyranoside **43** in 80% yield.

43: Syrup; $[\alpha]_D^{25}$ +84.2° (*c* 0.2); IR 1760 and 1740 (C=O), 1670 (C=C); ^{1}H NMR δ=8.14—7.26 (5H, m, Ph), 6.52 (1H, dd, $J_{4,6}$=$J_{4,6'}$=1.5 Hz, H-4), 6.05 (1H, d, $J_{2,1}$=4.2 Hz, H-2), 5.03 (1H, d, H-1), 4.82 (1H, dd, $J_{6,6'}$=1.5 Hz, H-6), 4.76 (1H, dd, H-6′), 3.62 (3H, s, OMe), 2.28 and 1.93 (3H×2, each s, OAc×2), 1.77 (3H, s, C-Me). Found: C, 60.53; H, 5.72%. Calcd for $C_{19}H_{22}O_8$: C, 60.31; H, 5.86%.

Methyl 2,3,4-Tri-*O*-methyl-4-*C*-methyl-α-D-*xylo*-hex-5-enopyranoside (45). After a mixture of methyl 2,3,4-tri-*O*-methyl-4-*C*-methyl-6-*O*-*p*-tolylsulfonyl-α-D-glucopyranoside **44** (600 mg, 1.48 mmol), NaI (1.10 g, 7.34 mmol), and Bu_4NI (270 mg, 0.73 mmol) in DMSO (80 cm^3) was stirred under argon in the presence of molecular sieves 4A (20 pieces) at 120°C for 12 h, DBU (1.10 g, 7.24 mmol) was added and kept at 120°C until the disappearance of 6-iodo derivative on TLC (for 12 h). A similar work up of the reaction mixture as in the case of compound **32** gave **45** in 91% yield.

45: Syrup; $[\alpha]_D^{26}$ +119° (*c* 1.4); IR 1680 (C=C); ^{1}H NMR δ=4.84 (1H, d, $J_{1,2}$=3.5 Hz, H-1), 4.70 (1H, d, $J_{6,6'}$=0.7 Hz, H-6), 4.66 (1H, d, H-6′), 3.88 (1H, d, $J_{3,2}$=9.5 Hz, H-3), 3.34 (1H, dd, H-2), 3.63, 3.54, 3.46, and 3.38 (3H×4, each s, OMe×4), 1.37 (3H, s, C-Me). Found: C, 56.93; H, 8.42%. Calcd for $C_{11}H_{20}O_5$: C, 56.88; H, 8.68%.

Methyl 2,3,4-Tri-*O*-methyl-4-*C*-methyl-6-*O*-*p*-tolylsulfonyl-α-D-glucopyranoside (44). MeI (1.3 equiv) was added dropwise to a mixture of methyl 2,3-di-*O*-methyl-4-*C*-methyl-6-*O*-triphenylmethyl-α-D-glucopyranoside[12] and NaH (1.2 equiv) in DMF at 0°C; the resulting mixture was kept at room temperature until the disappearance of the starting material. The reaction mixture was poured into a saturated NH_4Cl solution, extracted with ethyl acetate, and evaporated to give syrupy crude methyl 2,3,4-tri-*O*-methyl-4-*C*-methyl-6-*O*-triphenylmethyl-α-D-glucopyranoside. A 70% acetic acid solution of the above mentioned 2,3,4-tri-*O*-methyl derivative was stirred at 60°C to give the corresponding 6-hydroxy derivative. The yield was 82% (2 steps) after purification. A reaction of the above mentioned 6-hydroxy compound (3.0 g) with *p*-toluenesulfonyl chloride (2.6 g, 1.2 equiv) in pyridine was carried out for 12 h. The reaction mixture was poured into water, extracted with ethyl acetate, and evaporated to give the 6-*O*-*p*-tolylsulfonyl derivative **44**, which was recrystallized from ethanol–hexane. The yield was 80%.

44: Mp 80—81°C; $[\alpha]_D^{25}$ +94.2° (*c* 1.2); ^{1}H NMR δ=7.80 and 7.30 (4H, ABq, Ph), 4.74 (1H, d, $J_{1,2}$=3.9 Hz, H-1), 4.30 (1H, dd, $J_{5,6}$=10.0 Hz, $J_{5,6'}$=1.2 Hz, H-5), 4.03 (1H, dd, $J_{6,6'}$=8.8 Hz, H-6), 3.88 (1H, dd, H-6′), 3.14 (1H, dd, $J_{2,3}$=10.0 Hz, H-2), 3.57, 3.47, 3.38, and 3.32 (3H×4, each s, OMe×4), 2.42 (3H, s, Ph-Me), 1.08 (3H, s, C-Me). Found: C, 53.46; H, 6.96%. Calcd for $C_{18}H_{28}O_8S$: C, 53.45; H, 6.98%.

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