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STEREOSELECTIVE SYNTHESIS OF 3-(D-GLYCOPYRANOSYL)PROPENES BY USE OF ALLYLSILANES*

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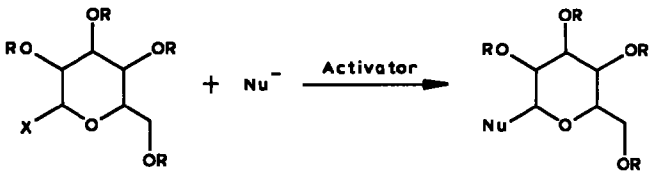
ABSTRACT

Reactions of allylsilanes with methyl pyranosides and pyranosyl chlorides proceeded very smoothly in the presence of a catalytic amount of trimethylsilyl trifluoromethanesulfonate and iodosilane to give the corresponding glycopyranosyl-3-propenes in highly stereoselective mode. The configuration depends upon the structure of allylsilanes. 2-Bromo-2-propenyltrimethylsilane, the lowest nucleophile among the allylsilanes used, afforded an almost pure *C*-α-D-glycosyl compound.

INTRODUCTION

Recently, much attention[1,2] has been focused on the stereoselective synthesis of pyranosyl and furanosyl compounds substituted by a functionalized alkyl group at C-1[2,3], since the products of the reaction can be used not only as chiral building blocks for the synthesis of naturally occurring compounds[4], but also as precursors to biologically active *C*-nucleosides and enzyme inhibitors, and as subunits of natural products[5]. In this direction, a number of efforts are currently being devoted to the direct formation of a carbon–carbon bond at the anomeric center of carbohydrates[6] (Scheme 1). Although the stereoselectivity depends upon the nature of the nucleophile reagent and leaving group, the activator also plays an important role in the functionalized alkylation using organosilicon reagents. We have recently



Scheme 1

*Chemistry of Organosilicon Compounds No. 218. A preliminary communication has been reported[1].
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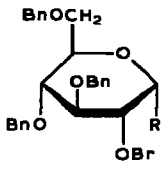
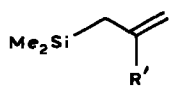
shown that α,α-diheteroatom-substituted alkanes (R^1R^2CXY; X, Y = RO, RS, R_2N, and Hal) are activated chemoselectively by trimethylsilyl trifluoromethanesulfonate (Me_3SiOTf) (**9**) and iodotrimethylsilane (**10**) to react with silyl enol ethers, ketene silyl acetals, and allylsilanes[7–10] and, especially, cyclic α-chloroethers, such as 2-chlorooxolane and 2-chlorooxane (α-chlorotetrahydropyran) display high reactivity towards allylsilanes[7,8]. Moreover, during the present work, we have found that the method can be applied to the activation of *N*-(trimethylsilylmethyl)aminomethyl ethers that function as efficient synthons for synthetically important, nonstabilized azomethine ylides[11].

We report herein the use of allylsilanes as excellent reagents for the stereoselective introduction of functionalized allyl groups at the anomeric center of carbohydrates in the presence of Me_3SiOTf (**9**) (ref. 12) and iodosilane (**10**).



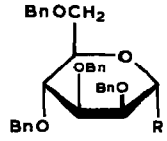
1 R = OMe
2 R = Cl

+

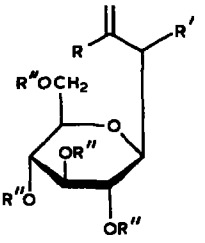


5 R = R' = H
6 R = H, R' = Me
7 R = Me, R' = H
8 R = H, R' = Br

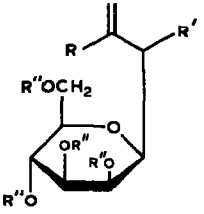
Me3SiOTf (9)
or Me3SiI (10)



3 R = OMe
4 R = Cl



11 R = R' = H, R" = Bn
12 R = Me, R' = H, R" = Bn
13 R = H, R' = Me, R" = Bn
14 R = Br, R' = H, R" = Bn
15 R = Me, R' = H, R" = Ac
16 R = Br, R' = H, R" = Ac



17 R = R' = H, R" = Bn
18 R = Me, R' = H, R" = Bn
19 R = Br, R' = H, R" = Bn
20 R = Br, R' = H, R" = Ac

RESULTS AND DISCUSSION

The reaction of 2-propenyltrimethylsilane (**5**) with methyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside (**1**) proceeded very smoothly in the presence of

Me_3SiOTf (**9**) in acetonitrile to give, highly stereoselectively in good yield, the α-D-glucopyranosylpropene **11**. The results and those with other allylsilanes (**6–8**) are summarized in Table I. The choice of solvent and the amount of activator are important for the success of this reaction. Thus, acetonitrile gave the most satisfactory results whereas dichloromethane, which is the most commonly used solvent for the activation of α,α-diheteroatom-substituted alkanes[7–10], was not suitable for the reaction. Although less than 10 mol of the catalyst **9** or **10**/100 mol had been sufficient previously to activate α,α-dihetereoatom-substituted alkanes, the present reaction required 20–50 mol of **9**/100 mol, presumably owing to interaction with other oxygen-functional groups in the molecule, in addition to the activation of the anomeric methoxy group. Apparently, **9** is a more efficient catalyst than **10** since the latter is known as a reagent for bond cleavage of the ether linkage[13].

Compound **11** could be obtained from the reaction of **5** with 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl chloride (**2**) catalyzed by **9** in a ratio of the two stereoisomers (α:β, 91:9) approximately similar to that obtained from **1**. In this case, even less than 20 mol of **9**/100 mol as the activator was sufficient to complete the catalytic cycle. Apparently the pyranosyl chloride was a more reactive substrate under the present allylation conditions, though the stereoselectivity was unchanged.

TABLE I

STEREOSELECTIVE SYNTHESIS OF 3-(D-GLYCOPYRANOSYL)PROPENES

Reactant	*Allylsilane*	*Conditions*		*Product*	*Yield (%)*[a]	*Ratio α- to β-D anomer*[b]
		Activator	*Time (h)*			
1	**5**	**9**	16	**11**	86	(91:9)
1	**5**	**9**	35[c]	**11**	54(23)	(91:9)
1	**5**	**9**	68[d]	**11**	Trace	(91:9)
1	**5**	[e]	48	**11**	24	(91:9)
1	**5**	**10**	27	**11**	60(22)	(91:9)
1	**6**	**9**	10	**12**	87	(86:14)
1	**7**	**9**	24	**13**	68	[f]
1	**8**	**9**	16	**14**	71	(100:0)
2	**5**	**9**	6.5	**11**	81	(91:9)
2	**5**	**10**	16	**11**	75	(91:9)
3	**5**	**9**	25	**17**	87	(100:0)
3	**5**	**10**	23	**17**	68(20)	(100:0)
3	**6**	**9**	8	**18**	81	(89:11)
3	**8**	**10**	12	**19**	45(35)	(100:0)
4	**5**	**9**	4	**17**	80	(100:0)
4	**8**	**10**	20	**19**	65	(100:0)

[a]Recovered **1** is shown in parentheses. [b]Determined by l.c. [c]20 mol% of **9**/100 mol was used. [d]The reaction was conducted in dichloromethane. [e]$BF_3 \cdot OEt_2$ was used as the activator. [f]Presumably **13** was a mixture of four diastereoisomers.

Methyl 2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranoside (**3**) and 2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl chloride (**4**) also reacted with allyltrimethylsilane (**5**), when very smoothly catalyzed by **9** and **10**, to afford the corresponding *C*-mannopyranosyl compound **17** with high stereoselectivity. The β-D anomer could not be detected by chromatographic and spectroscopic analysis.

From the results obtained with **1**, it could be concluded that the configuration at C-1 depends significantly upon the structure of the allylsilanes, but not upon the leaving group and the catalyst. Thus, use of 2-bromo-2-propenyltrimethylsilane[14] (**8**) resulted in a high selectivity for the α-D configuration at C-1 of **1**, whereas the β-D selectivity increased slightly with 2-methyl-2-propenyltrimethylsilane (**6**). However, it is important to point out that the β-D anomer was preponderant in all cases. The main factors controlling the configuration at C-1 in the present reaction are: (a) the stereoelectronic effect due to the lone-pair electrons of the ring oxygen atom, (b) the solvent effect, (c) the nature of the nucleophilic reagent, and (d) the steric effect.

Since the stereoselectivity of the products did not depend upon the leaving group at C-1 and the catalyst, it is reasonable to assume that the free oxonium ion **21** is the intermediate and that the nucleophilic attack of the allylsilanes **5–8** to give **22** takes place from the axial direction owing to the stereoelectronic effect[15] (Scheme 2). Moreover, undoubtedly acetonitrile accelarated the formation of the free oxonium ion (**21**) owing to the association of the solvent.

21 **22**

Scheme 2

The third condition for stereocontrol, the reactivity of the nucleophilic reagents, may also be considered. The α-D selectivity was decreasing gradually with the increasing nucleophilicity of the allylsilanes, in the order **6** > **5** > **8**. The nucleophilicity of **5–8** was determined by the following competitive experiment. When a mixture of a large excess of **5**, **6**, and **8** was treated with benzaldehyde dimethylacetal, catalyzed by **9**, the corresponding allylated products, **23** and **24**, were obtained in 27 and 65% yield, respectively. 2-Bromo-4-methoxy-4-phenylbutene (**25**), which might have derived from **8**, could not be detected in the reaction mixture.

5, 6, 8 → PhCHCH$_2$CH=CH$_2$ + PhCHCH$_2$C=CH$_2$ + PhCHCH$_2$C=CH$_2$

OMe (**23**, 27%) | OMe, CH$_3$ (**24**, 65%) | OMe, Br (**25**, 0%)

The high stereoselectivity observed in the D-mannose rather than in the D-glucose series may be explained by the difference in steric hindrance of the benzyloxy group at C-2 between the two series. Thus, the reaction of both glucopyranosides and mannopyranosides with allylsilanes may be important in organic synthesis to obtain *C*-glycosylpropenes with the α-D configuration in a highly stereoselective mode.

The structures of these compounds could be readily assigned by comparing the spectral data and chromatographic behaviors with those of authentic samples. Furthermore, the configuration at C-1 was confirmed by 200-MHz, ^{1}H-n.m.r. spectroscopy. Thus, after the major stereoisomer of the tetrabenzyl derivatives **11–14** and **17–19** was isolated from the reaction mixture by l.c., it was converted into its tetraacetate by hydrogenolysis in the presence of palladium–carbon followed by acetylation with acetic anhydride and pyridine. (See Experimental for **15** and **16**). The tetraacetate was purified by t.l.c. On the basis of the $J_{1,2}$ value (~6 Hz) of the 200-MHz, ^{1}H-n.m.r. spectrum, the acetate was characterized as an α-D anomer, the $J_{1,2}$ value of the α-D anomer being smaller than that of the β-D anomer[3]. Thus, the preponderant compounds of the reaction were the α-D anomers. The ^{1}H-n.m.r. data are quite similar to those of the products obtained by the addition reaction of a pyranosyl radical to acrylonitrile which gave α-D anomers[15]. Furthermore, the values of the specific rotations of the α-D anomers were larger than those of the β-D anomers, well in accord with the values for anomers in the D-series of carbohydrates[16].

EXPERIMENTAL

Methods. — Optical rotations were measured with an Union Tec. PM-101 automatic polarimeter. I.r. spectra were recorded with a Hitachi EPI-G2 spectrometer; ^{1}H-n.m.r. spectra with a Varian T-60, EM-390, and XL-200 spectrometers; and mass spectra with a JEOL JMS-300D GC-MS spectrometer.

Materials. — Allylsilanes[17–19] (**5–8**) and other organosilicon reagents[20,21] (**9, 10**) were prepared according to methods described in the literature. 2-Propenyltrimethylsilane (**5**) had b.p. 84.5–85.5°, lit.[17] 84.9° (98 kPa); and 2-methyl-2-propenyltrimethylsilane (**6**) b.p. 108°, lit.[18] 109° (100 kPa). 2-Butenyltrimethylsilane[19] (**7**), b.p. 6°, was prepared by the fluoride ion-promoted isomerization of a mixture of 2-methyl-2-propenylsilane and 2-butenylsilanes. Trimethylsilyl trifluoromethanesulfonate (**9**), b.p. 56–60° (3.5 kPa), lit.[20] 45–47° (2.3 kPa). Iodotrimethylsilane (**10**) was prepared, by an *in situ* method[21], from hexamethyldisilane and I_2. Compounds **1–4** were prepared by procedures cited in the literature[22–24].

2-Bromo-2-propenyltrimethylsilane (**8**). — 2,3-Dibromopropene (120 g, 0.60 mol) was treated[25] with trichlorosilane (97.5 g, 0.72 mol) and triethylamine (61.0 g, 0.60 mol) in the presence of $CuCl_2$ (3.0 g, 0.03 mol) in dry ether (250 mL). The resulting ammonium salt was removed by filtration and the filtrate was methylated with an excess of methylmagnesium bromide in ether. After work-up, pure **8** (66.4 g, 0.35 mol) was obtained by distillation (57% yield), b.p. 74–75° (87 kPa); lit.[25]

64–65°) (52 kPa); $\nu_{max}^{CCl_4}$ 3060 (m), 1670 (s), 1300 (s), 1240 (m), 1210 (m), 1130 (m), and 900 cm^{-1} (s); ^{1}H-n.m.r. (60 MHz, CCl_4): δ 0.19 (s, 9 H), 2.17 (m, 2 H), and 5.19 (m, 1 H); m.s.: *m/z* 194 (6), 192 (M^+, 6), 139 (27), 74 (9), 73 (100), and 45 (10).

C-Allylation of compounds **1–4**. — *General procedure.* In a 50-mL flask, equipped with a dropping funnel and a Dimroth condenser with a drying tube, were placed, under an N_2 atmosphere, compounds **1**, **2**, **3**, or **4** (1.5 mmol), an allylsilane (4 mmol) and dry acetonitrile (5 mL). Trimethylsilyl triflate (**9**) (0.15 g, 0.7 mmol) was added with a syringe and the mixture was stirred at room temperature for a given period, as shown in Table I. After the solution had been cooled to 0°, pyridine (a few drops) was added, the mixture hydrolyzed with saturated $NaHCO_3$, and then extracted with ether. The organic layer was washed with water, followed by saturated NaCl, and dried (Na_2SO_4). The solvent was removed under reduced pressure and the crude product purified by t.l.c. on silica gel to give a mixture of stereoisomers. A similar procedure was used with iodotrimethylsilane (**10**) as a catalyst. Each stereoisomer was isolated by l.c. In general, the α-D anomer was eluted after the β-D anomer.

*3-(2,3,4,6-Tetra-*O*-benzyl-*D*-glucopyranosyl)propene*[3] (**11**). — T.l.c. (4:1 benzene–ether) R_F 0.85.

α-D Anomer. $[\alpha]_D^{21}$ +32.1° (*c* 0.97, chloroform); ν_{max}^{KBr} 3070 (w), 2910 (s), 2870 (m), 1450 (m), 1360 (m), 1100 (s), 1080 (s), 1025 (m), 995 (m), 950 (m), 910 (m), 755 (s), 735 (s), and 700 cm^{-1} (s); ^{1}H-n.m.r. (90 MHz, $CDCl_3$): δ 7.43–7.00 (bs, 20 H), 6.03–5.53 (m, 1 H), 5.23–4.30 (m, 9 H), 4.26–3.43 (m, 8 H), and 2.47 (br.t, 2 H, *J* 7.5 Hz).

β-D Anomer. $[\alpha]_D^{21}$ −152° (*c* 0.6, chloroform); ν_{max}^{KBr} 3065 (w), 3030 (w), 2900 (s), 2865 (s), 1445 (m), 1360 (m), 1100 (s), 1060 (s), 995 (m), 950 (m), 910 (m), 740 (s), and 700 cm^{-1} (s); ^{1}H-n.m.r. (90 MHz, $CDCl_3$): δ 7.40–7.00 (br.s, 20 H), 6.23–5.67 (m, 1 H), 5.23–4.37 (m, 9 H), 3.83–3.17 (m, 8 H), and 2.80–2.10 (m, 1 H).

*2-Methyl-3-(2,3,4,6-tetra-*O*-benzyl-*D*-glucopyranosyl)propene* (**12**). — T.l.c. (4:1 benzene–ether) R_F 0.85.

α-D Anomer. $[\alpha]_D^{21}$ +21.7° (*c* 2.0, chloroform); ν_{max}^{KBr} 3050 (w), 3020 (m), 2890 (s), 2845 (s), 1595 (w), 1485 (w), 1440 (m), 1350 (m), 1200 (m), 1090 (s), 900 (m), 730 (s), and 695 cm^{-1} (s); ^{1}H-n.m.r. (90 MHz, $CDCl_3$): δ 7.37–7.00 (br.s, 20 H), 5.00–4.07 (m, 11 H), 3.87–3.43 (m, 6 H), 2.70–2.16 (m, 2 H), and 1.73 (s, 3 H).

β-D Anomer. $[\alpha]_D^{21}$ +5.0° (*c* 0.8, chloroform); ν_{max}^{KBr} 3060 (w), 3030 (w), 2900 (m), 1490 (w), 1445 (m), 1360 (w), 1085 (bs), 735 (s), and 695 cm^{-1} (s); ^{1}H-n.m.r. (90 MHz, $CDCl_3$): δ 7.33–7.06 (bs, 20 H), 4.96–4.50 (m, 10 H), 3.73–3.23 (m, 7 H), and 2.70–2.00 (m, 2 H), 1.78 (s, 3 H).

Anal. Calc. for $C_{38}H_{42}O_5$: C, 78.86; H, 7.31. Found: C, 78.80; H, 7.46.

*3-(2,3,4,6-Tetra-*O*-benzyl-*D*-glucopyranosyl)butene* (**13**). — T.l.c. (2:1 hexane–ether) R_F 0.75; ^{1}H-n.m.r. (90 MHz, $CDCl_3$): δ 7.30–7.20 (br.s, 20 H), 6.10–5.55 (m, 1 H), 5.20–4.85 (m, 2 H), 4.70–4.55 (m, 8 H), 4.00–3.70 (m, 7 H), 2.70–3.00 (m, 1 H), and 1.15 (t, 3 H, *J* 7.0 Hz). Two stereoisomers could be separated in the ratio of ~2:3 by l.c. However, it was impossible to assign their structures

since four stereoisomers (two diastereomers of α- and β-D anomers) could be present in the reaction mixture.

2-Bromo-3-(2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyl)propene (**14**). — T.l.c. (2:1 hexane–ether) R_F 0.50; ν_{max}^{KBr} 3060 (w), 3030 (m), 2910 (m), 2850 (m), 1625 (m), 1445 (m), 1125 (s), 1090 (s), 1060 (s), 1000 (s), 900 (w), 750 (s), and 695 cm^{-1} (s); ^{1}H-n.m.r. (90 MHz, $CDCl_3$): δ 7.33–7.00 (br.s, 20 H), 5.63–5.52 (m, 1 H), 5.47–5.40 (m, 1 H), 4.86–4.27 (m, 9 H), 3.80–3.10 (m, 6 H), and 2.90–2.70 (m, 2 H).

Anal. Calc. for $C_{37}H_{39}BrO_5$: C, 69.05; H, 6.12; Br, 12.41. Found: C, 68.68; H, 6.26; Br, 12.67.

3-(2,3,4,6-Tetra-O-benzyl-α-D-mannopyranosyl)propene (**17**). — T.l.c. (4:1 benzene–ether) R_F 0.85; $[\alpha]_D^{21}$ −3.0° (*c* 7.0, chloroform); ν_{max}^{film} 3070 (m), 3035 (m), 1369 (m), 1205 (m), 1100 (s), 1030 (m), 915 (m), 790 (s), 760 (s), and 700 cm^{-1} (s); ^{1}H-n.m.r. (90 MHz, CCl_4): δ 7.33–7.03 (br.s, 20 H), 6.03–5.53 (m, 1 H), 5.13–4.86 (m, 2 H), 4.73–4.33 (m, 7 H), 4.10–3.53 (m, 8 H), and 2.30 (br.t, 2 H, *J* 7 Hz).

2-Methyl-3-(2,3,4,6-tetra-O-benzyl-α-D-mannopyranosyl)propene (**18**). — T.l.c. (2:1 hexane–ether) R_F 0.60.

α-D Anomer. $[\alpha]_D^{21}$ +4.7° (*c* 3.8, chloroform); ^{1}H-n.m.r. (90 MHz, $CDCl_3$): δ 7.37–6.93 (m, 20 H), 5.10–3.30 (m, 17 H), 2.32 (br.t, 2 H, *J* 6.8 Hz), and 1.70 (s, 3 H).

β-D Anomer. $[\alpha]_D^{21}$ −22° (*c* 0.9, chloroform); ^{1}H-n.m.r. (90 MHz, $CDCl_3$): δ 7.33–7.00 (m, 20 H), 4.83–3.56 (m, 17 H), and 2.31 (br.d, 2 H, *J* 7.5 Hz).

Anal. Calc. for $C_{38}H_{42}O_5$: C, 78.86; H, 7.31. Found: C, 78.60; H, 7.57.

2-Bromo-3-(2,3,4,6-tetra-O-benzyl-α-D-mannopyranosyl)propene (**19**). — T.l.c. (2:1 hexane–ether) R_F 0.45; ν_{max}^{film} 3080 (w), 3060 (w), 3020 (m), 2900 (s), 2860 (s), 1660 (w), 1450 (m), 1100 (s), 740 (s), and 700 cm^{-1} (s); ^{1}H-n.m.r. (90 MHz, $CDCl_3$): δ 7.40–7.07 (br.s, 20 H), 5.60–5.50 (m, 1 H), 5.43–5.38 (m, 1 H), 4.76–4.20 (m, 9 H), 4.00–5.37 (m, 6 H), and 2.67 (br.d, 2 H, *J* 7.5 Hz).

2-Methyl-1-(2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl)propane (**15**). — Compound **12** (186 mg, 0.32 mmol), isolated by l.c. from the reaction mixture, was hydrogenated (0.1 MPa) in the presence of 10% Pd–C (80 mg) in methanol (10 mL) and acetic acid (2 mL) for 10 h at room temperature. After the catalyst and the solvent had been removed, acetic anhydride (10 mL) and pyridine (10 mL) were added. The mixture was stirred for 24 h at room temperature and then poured into ice–water (50 mL) and the product extracted with chloroform. The organic layer was washed with saturated $NaHCO_3$ several times, dried (Na_2SO_4), and the solvent removed. The residue was purified by t.l.c. (silica gel) to give **15** (78 mg, 0.20 mmol, 63%), t.l.c. (1:1 hexane.ether) R_F 0.30; ν_{max}^{KBr} 2960 (m), 1740 (s), 1380 (m), 1360 (m), 1230 (s), 1090 (m), and 1035 cm^{-1} (s); ^{1}H-n.m.r. (200 MHz, $CDCl_3$): δ 5.30 (dd, $J_{2,3}$ 9.1, $J_{3,4}$ 9.0 Hz, H-3), 5.07 (dd, $J_{2,3}$ 9.1, $J_{1,2}$ 5.8 Hz, H-2), 4.98 (dd, $J_{3,4} = J_{4,5}$ 9.0 Hz, H-4), 4.34–4.18 (m, H-1), 4.24 (dd, $J_{5,6}$ 5.0, $J_{6a,6b}$ 12.0 Hz, H-6a), 4.05 (dd, $J_{5,6b}$ 2.6, $J_{6a,6b}$ 12.0 Hz, H-6b), 3.88 (ddd, $J_{4,5}$ 9.0, $J_{5,6a}$ 5.0, $J_{5,6b}$ 2.6 Hz, H-5), 2.06 (s, 3 H), 2.02 (s, 3 H), 2.01 (s, 3 H), 2.00 (s, 3 H), 1.86–1.58 (m, 2 H),

1.28–1.10 (m, 1 H), 0.94 (d, 3 H, *J* 7.0 Hz), and 0.88 (d, 3 H, *J* 7.0 Hz).

Anal. Calc. for $C_{18}H_{28}O_9$: C, 55.66; H, 7.26. Found: C, 55.45; H, 7.20.

*2-Methyl-1-(2,3,4,6-tetra-*O*-acetyl-α-*D*-glucopyranosyl)propane*[3] (**16**). — This compound was pepared from 2-bromo-3-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)propene (**14**) (93 mg, 0.144 mmol) by a procedure similar to that described for the preparation of **15** (28 mg, 0.075 mmol), t.l.c. (1:1 hexane–ether) R_F 0.20; ^{1}H-n.m.r. (200 MHZ, $CDCl_3$): δ 5.36 (dd, $J_{2,3} = J_{3,4}$ 9.8 Hz, H-3), 5.11 (dd, $J_{1,2}$ 5.8, $J_{2,3}$ 9.8 Hz, H-2), 5.02 (dd, $J_{3,4} = J_{4,5}$ 9.8 Hz, H-4), 4.28 (dd, $J_{5,6a}$ 5.2, $J_{6a,6b}$ 12.0 Hz, H-6a), 4.26–4.16 (m, H-1), 4.10 (dd, $J_{5,6b}$ 3.0, $J_{6a,6b}$ 12.0 Hz, H-6b), 3.85 (ddd, $J_{4,5}$ 9.8, $J_{5,6a}$ 5.2, $J_{5,6b}$ 3.0 Hz, H-5), 2.10 (s, 3 H), 2.06 (s, 3 H), 2.04 (s, 3 H), 2.03 (s, 3 H), 1.90–1.85 (m, 1 H), 1.54–1.24 (m, 3 H), and 0.96 (*t*, *J* 7.0 Hz, 3 H); identical with the compound obtained from **11** by similar procedure.

Anal. Calc. for $C_{17}H_{26}O_9$: C, 54.54; H, 7.00. Found: C, 54.88; H, 7.24.

*1-(2,3,4,6-Tetra-*O*-acetyl-α-*D*-mannopyranosyl)propane*[3] (**20**). — This compound was prepared from **19** by a procedure similar to that described for the preparation of **15** in 71% yield, t.l.c. (1:1 hexane–ether) R_F 0.20; ^{1}H-n.m.r. (200 MHz, $CDCl_3$): δ 5.34–5.18 (m, 3 H), 4.34 (dd, 1 H, *J* 6.0, 12.0 Hz, 1 H), 4.12 (dd, 1 H, *J* 3.0, 12.0 Hz, H-1), 4.04–3.96 (m, 1 H), 3.94–3.80 (m, 1 H), 2.14 (s, 3 H), 2.10 (s, 3 H), 2.06 (s, 3 H), 2.02 (s, 3 H), 1.92–1.70 (m, 1 H), 1.64–1.30 (m, 3 H), and 0.96 (t, 3 H, *J* 7.0 Hz). On the basis of spectroscopic and chromatographic analysis, **20** was identical with the compound obtained[3] from the α-D anomer of **17**.

Competitive reaction of allylsilanes with benzaldehyde dimethylacetal. — A mixture of 2-propenyltrimethylsilane (**5**; 571 mg, 5.0 mmol), 2-methyl-2-propenyltrimethylsilane (**6**; 645 mg, 5.0 mmol), 2-bromo-2-trimethylsilane (**8**; 968 mg, 5.0 mmol), and benzaldehyde dimethylacetal (158 mg, 1.0 mmol) in dichloromethane (5 mL) was placed in a 50-mL flask and the flask cooled to −78°. To this was added, from a syringe, trimethylsilyl triflate (**9**; 20 mg, 0.1 mmol) and the mixture stirred for 8 h at −78°. After the usual workup, 4-methoxy-4-phenyl-1-butene[9] (**23**; 44 mg, 0.27 mmol) and 4-methoxy-2-methyl-4-phenyl-1-butene[9] (**24**; 115 mg, 0.65 mmol) were isolated by t.l.c. in 27 and 65% yield, respectively. No trace of 2-bromo-4-methoxy-4-phenyl-1-butene (**25**) was detected by g.l.c.

Compound **23**. T.l.c. (3:2 hexane–benzene) R_F 0.45; ^{1}H-n.m.r. (60 MHz, CCl_4): δ 7.33 (s, 5 H), 6.07–4.80 (m, 3 H), 4.10 (t, 1 H, *J* 7 Hz), 3.20 (s, 3 H), and 2.63–2.27 (m, 1 H); m.s.: *m/z* 121 (M^+ −41, 100%) and 77 (19%).

Compound **24**. T.l.c. (3:2 hexane–benzene) R_F 0.50; ^{1}H-n.m.r. (60 MHz, CCl_4): δ 7.20 (s, 5 H), 4.83–4.65 (m, 2 H), 4.20 (t, 1 H, *J* 10 Hz), 3.14 (s, 3 H), 2.33 (m, 2 H), and 1.70 (s, 3 H); m.s.: *m/z* 121 (M^+ −55, 25%), 119 (89%), and 117 (100%).

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