The Use of Grignard Reagents in the Synthesis of Carbohydrates. II.[1] The Cleavage of Acetal Protecting Groups in Sugar Derivatives

Masajiro KAWANA* and Sakae EMOTO

The Institute of Physical and Chemical Research, Wako-shi, Saitama 351

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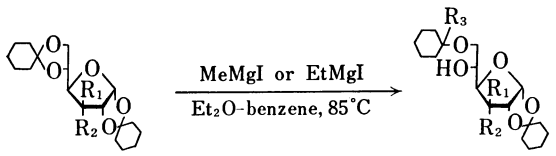
The selective reaction of acetal protecting groups in sugars with Grignard reagents is described. The treatment of 1,2:5,6-di-*O*-cyclohexylidene-α-D-glucofuranose (**1**) with methylmagnesium iodide in benzene–ether at about 85 °C gave 1,2-*O*-cyclohexylidene-6-*O*-(1-methylcyclohexyl)-α-D-glucofuranose. When isopropylmagnesium iodide or *t*-butylmagnesium bromide was used instead of methylmagnesium iodide, **1** gave 1,2-*O*-cyclohexylidene-6-*O*-(cyclohex-1-enyl)-α-D-glucofuranose and the corresponding 6-*O*-cyclohexyl derivative. The selective cleavage of the acetal protecting groups in some other sugars with the Grignard reagents is also described.

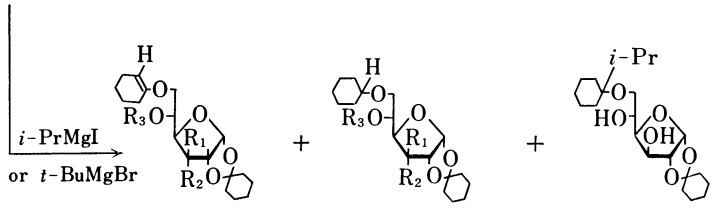
It is considered that acetals are generally stable under Grignard reaction conditions. However, when benzene was used as a solvent, the Grignard reagent formed a complex with the acetal, resulting in the cleavage of the acetal carbon–oxygen bond.[2] For example, the treatment of 1,4-dioxaspiro[4.5]decane (cyclohexanone ethylene acetal) with methylmagnesium iodide (MeMgI) in a benzene solution at 75 °C gave 2-(1-methylcyclohexyloxy)ethanol in a 91% yield.[2a] In the course of our work on the synthesis of sugar derivatives with Grignard reagents, we found that the acetal protecting groups in the sugar derivatives were also cleaved by these reagents to be transformed into *O*-alkyl or -alkenyl protecting groups. Independently, Fischer and Horton[3] have found a similar phenomenon in the carbohydrate field. They treated 1,2:5,6-di-*O*-isopropylidene-α-D-*ribo*-hexofuranos-3-ulose with phenylmagnesium bromide under usual Grignard reaction conditions to obtain two normal Grignard adducts, along with a small amout of the 5,6-*O*-isopropylidene ring-opening product. In this paper we wish to describe our results concerning the cleavage of cyclohexylidene and isopropylidene groups in the sugars with several kinds of Grignard reagents.

When a mixture of 1,2:5,6-di-*O*-cyclohexylidene-α-D-glucofuranose[4] (**1**) and 4 molar equivalent of MeMgI in benzene–ether was heated under reflux at about 85 °C (Method A, Table 1) for 20 h, the 5,6-*O*-cyclohexylidene group of **1** was selectively cleaved and the methyl group of the Grignard reagent was introduced into the cyclohexyl moiety to form 1,2-*O*-cyclohexylidene-6-*O*-(1-methylcyclohexyl)-α-D-glucofuranose (**3**) in a 58% yield (Fig. 1); under these reaction conditions, the ether had very gradually been evaporated through a refluxing condenser. Its reaction time was shortened to about 1 h when the reaction mixture in a flask without a refluxing condenser was heated at the same temperature and the ether was allowed to evaporate (Method B).

The structural assignment of **3** was done on the basis of its elemental analysis and spectral properties (Tables 2 and 3). The ^{1}H NMR spectrum of **3** in dimethyl-d_6 sulfoxide showed a singlet at δ 1.04 due to the methyl protons and two doublets at δ 4.50 and 5.07 due to two secondary hydroxyl protons. The signals due to the methylene protons at C-6 for **3** shifted by *ca.* 0.3 ppm to a higher field than those for **1**. This shift was diagnostic for the *O*-alkylation at C-6 of the aldohexofuranoses prepared in the present work. On the other hand, the chemical shifts and coupling constants of the anomeric and C-2 protons of **3** were



1 : R_1=OH; R_2=H
2 : R_1=H; R_2=OH
3 : R_1=OH; R_2=H; R_3=Me
4 : R_1=OH; R_2=H; R_3=Et
5 : R_1=H; R_2=OH; R_3=Me



6 : R_1=OH; R_2, R_3=H
7 : R_1=OAc; R_2=H; R_3=Ac
8 : R_1=H; R_2=OH; R_3=H
9 : R_1=OH; R_2, R_3=H
10 : R_1=OAc; R_2=H; R_3=Ac
11 : R_1=H; R_2=OH; R_3=H
12

Fig. 1.

Table 1. The reactions of the sugar derivatives with the Grignard reagents

Starting material (mmol)	Reagent (mmol)	Solvent[a] benzene–ether (ml)	Method[b]	Reaction time h	Product	Yield %	Chromatography[c] benzene–AcOEt (v/v)
1 (2)	MeMgI (8)	10—10	A	20	**3**	58	($CHCl_3$)
1 (1)	MeMgI (4)	15—5	B	1.25	**3**	67	($CHCl_3$)
1 (1)	EtMgI (4)	15—5	B	1.4	**4**	67	8 : 2
1 (2)	*i*-PrMgI (8)	30—10	B	1.3	**6** 60 **9** 11 **12** 8		7 : 3
1 (1)	*t*-BuMgBr (8)	15—10	B	0.6	**6**[d]	(87)	—
2 (2)	MeMgI (8)	10—10	A	6.8	**5**	75	($CHCl_3$)
2 (1)	MeMgI (4)	15—5	B	0.5	**5**	84	85 : 15
2 (1)	*i*-PrMgI (4)	15—5	B	0.7	**8** 53 **11** 14		8 : 2
2 (1)	*t*-BuMgBr (16)	30—20	B	0.3	**11**	92	7 : 3
13 (3)	MeMgI (12)	10—10	A	6	**15**	79	8 : 2
13 (1)	MeMgI (4)	15—5	B	1.2	**15**	54	7 : 3
14 (3)	MeMgI (12)	10—10	A	3.8	**16**	54	1 : 1
14 (1)	MeMgI (4)	15—5	B	0.2	**16**	56	1 : 1
17 (1)	MeMgI (4)	5—5	A	3	**19**	73	8 : 2
18 (0.19)	MeMgI (1.6)	5—5	A	4	**20**	64	9 : 1
21 (3)	MeMgI (12)	10—10	A	20	**22**	58	9 : 1
21 (2)	*i*-PrMgI (8)	10—20	B	1.75	**23a** 52 **24a** 22		8 : 2
21 (1)	*t*-BuMgBr (8)	20—10	B	2	**23a** 21 **24a** 71		8 : 2

a) Anhydrous solvents were used. b) A: A reaction mixture in a flask equipped with a condenser was refluxed at 80—85 °C for the given reaction time. B: A reaction mixture was heated at the same temperature without a refluxing condenser to remove the ether by distillation. c) Crude products were purified by chromatography on a silica-gel column with the given solvent system. d) This product was not isolated, acetylated to **7** (see Experimental).

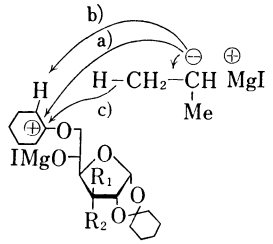
almost the same as those for **1**, thus indicating that the 1,2-*O*-cyclohexylidene moiety of **1** was unchanged in this product. These observations were consistent with the proposed structure for **3**.

The reaction of **1** with ethylmagnesium iodide similarly gave a 1-ethylcyclohexyl derivative (**4**). Using isopropylmagnesium iodide (*i*-PrMgI), however, we obtained 6-*O*-cyclohexenyl and -cyclohexyl[5] derivatives (**6** and **9**) in 60 and 11% yields respectively, along with a small amount of a 6-*O*-(1-isopropylcyclohexyl) derivative (**12**).

The compound (**6**), with the enol group, could not be purified because of its instability at room temperature. When *t*-butylmagnesium bromide (*t*-BuMgBr) was used in this reaction, **6** was also produced; it was later acetylated to give the corresponding diacetyl derivative (**7**) in an 87% overall yield. The ^1H NMR spectrum of **7** showed a multiplet at δ 4.60 due to a vinyl proton at C-2′. On catalytic hydrogenation, **7** was converted into 3,5-di-*O*-acetyl-6-*O*-cyclohexyl-1,2-*O*-cyclohexylidene-α-D-glucofuranose (**10**), which was identical with the specimen prepared from **9** by acetylation.

Similarly, 1,2:5,6-di-*O*-cyclohexylidene-α-D-allofuranose[6] (**2**) reacted with MeMgI to yield a 6-*O*-(1-methylcyclohexyl) derivative (**5**). When **2** was treated with *i*-PrMgI, a 6-*O*-cyclohexenyl derivative (**8**) was obtained in a good yield as crystals, which could be purified by recrystallization.

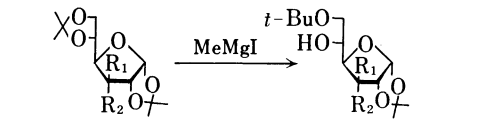
The formation of 6-*O*-alkyl and -alkenyl derivatives can be explained by means of a postulated intermediacy (**A**), which involves a cyclohexyl cation[2b] formed



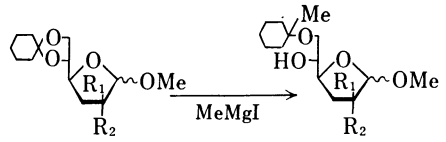
A

by the ring-opening of the 5,6-*O*-cyclohexylidene group. The attack of the alkyl anion of the Grignard reagent on the center of this cation (Path a) gave the 1-alkylcyclohexyl derivatives (**3**—**5** and **12**). When a sterically bulky reagent, such as *i*-PrMgI or *t*-BuMgBr, was used in this reaction, the direct attack of the bulky alkyl group of this reagent on the center of the cyclohexyl cation was largely prevented, so that the abstraction of a proton α to the cation (Path b) and the reduction of this cation (Path c) by the reagent preferably occurred to afford the cyclohexenyl compounds (**6** and **8**) and the cyclohexyl compounds (**9** and **11**) respectively.

The isopropylidene groups also reacted with the Grignard reagents. Thus, the treatment of 1,2:5,6-



13 : R_1=OH; R_2=H 15 : R_1=OH; R_2=H
14 : R_1=H; R_2=OH 16 : R_1=H; R_2=OH



17 : R_1=OH; R_2=Me; (β) 19 : R_1=OH; R_2=Me; (β)
18 : R_1=Me; R_2=OH; (α) 20 : R_1=Me; R_2=OH; (α)

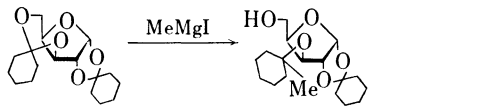
Fig. 2.

di-*O*-isopropylidene-α-D-gluco-[7] and -allofuranose[8] (**13** and **14**) with MeMgI gave the corresponding 6-*O*-*t*-butyl derivatives (**15** and **16** respectively) (Fig. 2). Here again, the 1,2-*O*-isopropylidene group remained intact, but the one at the 5,6-position was selectively cleaved, while the secondary hydroxyl group at C-5 was freed. This selectivity was the same as that observed by Fischer and Horton.[3]

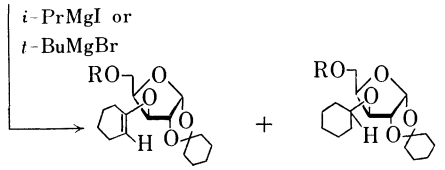
Branched-chain deoxy sugars, [1a,9] methyl 5,6-*O*-cyclohexylidene-3-deoxy-2-*C*-methyl-β-D-*arabino*-hexofuranoside (**17**), and the corresponding α-D-*ribo* isomer (**18**) yielded, upon treatment with MeMgI, the corresponding 6-*O*-(1-methylcyclohexyl) derivatives, **19** and **20** respectively.

The same reaction was applied to an acetal protecting aldopentose; 1,2:3,5-di-*O*-cyclohexylidene-α-D-xylofuranose[10] (**21**) reacted with MeMgI to give 1,2-*O*-cyclohexylidene-3-*O*-(1-methylcyclohexyl)-α-D-xylofuranose (**22**) in a 58% yield (Fig. 3). The cleavage of the carbon–oxygen bond between O-5 and the cyclohexyl carbon in **21** was confirmed by means of ^{1}H NMR spectroscopy. On the treatment of **21** with *i*-PrMgI, 3-*O*-(cyclohex-1-enyl)-1,2-*O*-cyclohexylidene-α-D-xylofuranose (**23a**) was obtained as the main product (52%), but with *t*-BuMgBr the corresponding 3-*O*-cyclohexyl derivative (**24a**) was the major one (71%). The former product was characterized as its acetate (**23b**); thus, it was hydrogenated to give 5-*O*-acetyl-3-*O*-cyclohexyl-1,2-*O*-cyclohexylidene-α-D-xylofuranose (**24b**), which was identical with the sample prepared by the acetylation of **24a**.

In all cases of the aldohexofuranoses tested in the present experiments, their 5,6-*O*-acetal protecting groups were selectively cleaved and the secondary hydroxyl groups at C-5 were selectively freed. The latter selectivity is, however, different from that observed for the previously reported experiments with a steroidal derivative (**25**), in which the acetal ring was opened to form the primary hydroxyl group.[2b] It has been assumed that, in this case, the Grignard reagent would predominantly attack the sterically less hindered primary hydroxyl oxygen of the acetal ring. This is the case for the reaction of the pentofuranose (**21**). One possible explanation for the observed selectivity in the hexofuranose is as follows.



21 22

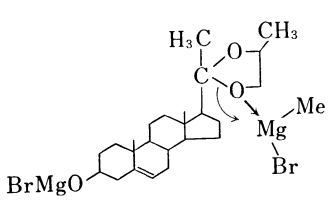


23 24

a : R=H
b : R=Ac

Fig. 3.

The magnesium atom of the Grignard reagent would be coordinated with both oxygen atoms of C-5 and the furanose ring (see **26**);[11] these oxygens were, therefore, activated to cleave the bond between O-5 and the cyclohexyl carbon in this case.[12] The same chelation as in **26** would also be possible for **21** to explain the observed selectivity.



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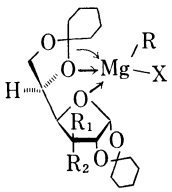

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Experimental

The melting points are uncorrected. The optical rotations were determined with a Perkin-Elmer 241 MC polarimeter. The IR spectra were recorded on a Shimadzu IR-27 instrument. The mass spectra were obtained with a Japan Optics Lab. Model JMS-OlSG instrument. The ^{1}H NMR spectra were recorded on a Varian HA-100D apparatus, with tetramethylsilane as the internal standerd. Merck silica gel GF_{254} was used for the TLC, and the compounds were detected by heating after spraying them with a methanol–sulfuric acid–*p*-methoxylbenzaldehyde (85:10:5, v/v) mixture. Merck silica gel 60 (0.063—0.29 mm) was used for column chromatography. The elemental analyses were performed by this Institute.

The results of the elemental analysis and the physical properties of the compounds obtained are summarized in Tables 2 and 3.

General Method for the Reaction of the Acetal Protecting Sugars with the Grignard Reagents. Some of the reaction conditions are described in Table 1. A crystalline sugar derivative or a solution of a syrupy sugar derivative in a small amount of dry benzene was added to a solution of the Grignard reagent in dry benzene–ether in a flask equipped with a condenser (Method A) or without a condenser (Method B) at room temperature under a dry nitrogen atmosphere. The mixture was then heated at 80—85 °C (bath temperature) for a given period; in the case of Method B, the ether was distilled out. After cooling, aqueous ammonium chloride was added, and the mixture was extracted with ether. The extract was washed with water, dried ($MgSO_4$), and con-

Table 2. The spectral data (MS, IR, and ^{1}H NMR) of the products

Product	MS, *m/e* (M^+)	IR(neat) (cm^{-1})	^{1}H NMR (δ)
3	356	—	DMSO-d_6: 1.04(3H, s, CH_3), 1.0—1.9(20H, m, cyclohexane ring protons), 3.1—3.5(2H, m, H-6), 4.36(1H, d, J=3.8 Hz, H-2), 4.50(1H, d, J=6.4 Hz, OH), 5.07(1H, d, J=4.4 Hz, OH), 5.79(1H, d, J=3.8 Hz, H-1)
4	370	—	$CDCl_3$: 0.82(3H, t, J=7.2 Hz, CH_3), 1.0—1.2(22H, m, cyclohexane ring protons and $CH_3C\underline{H}_2$), 3.3—3.7 (2H, m, H-6), 4.53(1H, d, J=4.0 Hz, H-2), 5.97 (1H, d, J=4.0 Hz, H-1)
5	356	—	DMSO-d_6: 1.04(3H, s, CH_3), 1.1—1.2(20H, m, cyclohexane ring protons), 3.1—3.5(2H, m, H-6), 4.44(1H, t, J=4.0 Hz, H-2), 4.64(1H, d, J=5.0 Hz, OH), 4.69(1H, d, J=6.4 Hz, OH), 5.65(1H, d, J=4.0 Hz, H-1)
6	—	1672 (C=C)	$CDCl_3$: 1.2—2.2(18H, m, CH_2 of cyclohexane and cyclohexene rings), 3.16(1H, br d, J=3.6 Hz, OH), 3.54 (1H, br s, OH), 4.52(1H, d, J=3.7 Hz, H-2), 4.68 (1H, m, vinyl proton), 5.96(1H, d, J=3.7 Hz, H-1)
7	427	1755 (C=O) 1672 (C=C)	$CDCl_3$: 1.2—2.2(18H, m, CH_2 of cyclohexane and cyclohexene rings), 2.00 and 2.04(3H, each s, CH_3), 3.82 and 3.95(1H, each q, H-6), 4.48(1H, d, J=4.0 Hz, H-2), 4.60(2H, m, H-4 and vinyl proton), 5.22(1H, m, H-5), 5.38(1H, d, J=2.6 Hz, H-3), 5.92(1H, d, J=4.0 Hz, H-1)
8	340	1668[b] (C=C)	$CDCl_3$: 1.2—2.3(18H, m, CH_2 of cyclohexane and cyclohexene rings), 2.54(1H, d, J=3.3 Hz, OH), 2.76 (1H, d, J=8.6 Hz, OH), 4.5—4.8(2H, m, H-2 and vinyl proton), 5.81 (1H, d, J=4.0 Hz, H-1)
9	342	—	DMSO-d_6: 1.0—1.2(20H, m, CH_2 of cyclohexane ring), 3.1—3.7(3H, m, H-6 and CH of cyclohexane ring), 4.36 (1H, d, J=3.6 Hz, H-2), 4.62(1H, d, J=5.6 Hz, OH), 5.07(1H, d, J=4.8 Hz, OH), 5.79(1H, d, J= 3.6 Hz, H-1)
10	426	1743[b] (C=O)	$CDCl_3$: 1.0—2.0(20H, m, CH_2 of cyclohexane ring), 2.00 and 2.02(3H, each s, CH_3), 3.3(1H, m, CH of cyclohexane ring), 3.62 and 3.79(1H, each q, H-6), 4.46(1H, d, J=3.7 Hz, H-2), 5.1(1H, m, H-5), 4.37 (1H, d, J=2.6 Hz, H-3), 5.92(1H, d, J=3.7 Hz, H-1)
11	342	—	$CDCl_3$: 1.0—2.1(20H, m, CH_2 of cyclohexane rings), 1.69 (1H, d, J=3.8 Hz, OH), 3.34(1H, m, CH of cyclohexane ring), 3.44(1H, d, J=6.2 Hz, OH), 3.64(2H, m, H-6), 4.62(1H, t, J=4.0 Hz, H-2), 5.78(1H, d, J=4.0 Hz, H-1)
12	342	—	$CDCl_3$: 0.86(6H, d, J=6.6 Hz, $CH_3\times2$), 1.0—1.1(21H, m, CH_2 of cyclohexane rings and CH of isopropyl group), 3.23(1H, br d, J=3 Hz, OH), 3.3—3.36(2H, m, H-6), 3.78(1H, br d, J=3 Hz, OH), 4.52(1H, d, J=3.7 Hz, H-2), 5.96(1H, d, J=3.7 Hz, H-1)
15	261[a]	—	DMSO-d_6: 1.11(9H, s, *t*-butyl protons), 1.22 and 1.36(3H, each s, isopropylidene protons), 3.1—3.6(2H, m, H-6), 4.36(1H, d, J=4.0 Hz, H-2), 4.52(1H, d, J=5.5 Hz, OH), 5.06(1H, d, J=4.8 Hz, OH), 5.78(1H, d, J=4.0 Hz, H-1)

TABLE 2. Continued

Product	MS, *m/e* (M^+)	IR(neat) (cm^{-1})	^1H NMR (δ)
16	261[a]	—	DMSO-d_6: 1.11(9H, s, *t*-butyl protons), 1.26 and 1.44(3H, each s, isopropylidene protons), 3.14—3.54(2H, m, H-6), 4.45(1H, t, J=4.0 Hz, H-2), 4.65(1H, d, J=4.8 Hz, OH), 4.74(1H, d, J=7.2 Hz, OH), 5.64(1H, d, J=4.0 Hz, H-1)
19	288	—	DMSO-d_6: 1.05 and 1.16(3H, each s, CH_3), 1.1—2.1(12H, m, H-3 and CH_2 of cyclohexane ring), 2.0—3.6(3H, m, H-6 and H-5), 3.27(3H, s, CH_3), 3.85(1H, br q, H-4), 4.23(1H, s, H-1), 4.41(1H, d, J=5 Hz, OH at C-5), 4.43(1H, s, OH at C-2)
20	288	—	$CDCl_3$: 1.09(3H, s, CH_3 at C-1'), 1.34(3H, s, CH_3 at C-2), 2.0(2H, m, H-3), 2.54(1H, d, J=4.0 Hz, OH at C-5), 2.94(1H, s, OH at C-2), 3.2—3.4(2H, m, H-6), 3.44(3H, s, OCH_3), 3.72(1H, m, H-5), 4.2 (1H, m, H-4), 4.50(1H, s, H-1)
22	326	—	DMSO-d_6: 1.0—1.9(20H, m, CH_2 of cyclohexane rings), 1.13 (3H, s, CH_3), 4.41(1H, d, J=4.0 Hz, H-2), 4.51 (1H, t, J=5.6 Hz, OH), 5.79(1H, d, J=4.0 Hz, H-1)
23a	—	1673 (C=C)	DMSO-d_6: 1.0—2.2(18H, m, CH_2 of cyclohexane and cyclohexene rings), 3.58(2H, m, H-5), 4.47(1H, d, J= 4.0 Hz, H-2), 4.65(1H, t, J=5.6 Hz, OH), 4.75(1H, m, vinyl proton), 5.82(1H, d, J=4.0 Hz, H-1)
23b	352	1745 (C=O) 1670 (C=C)	$CDCl_3$: 1.1—2.2(18H, m, CH_2 of cyclohexane and cyclohexene rings), 2.08(3H, s, CH_3), 4.55(1H, d, J= 4.0 Hz, H-2), 4.78(1H, br t, vinyl proton), 5.95(1H, d, J=4.0 Hz, H-1)
24a	312	—	DMSO-d_6: 1.0—1.9(20H, m, CH_2 of cyclohexane rings), 3.37 (1H, m, CH of cyclohexane ring), 4.44(1H, d, J= 4.0 Hz, H-2), 4.56(1H, t, J=5.6 Hz, OH), 5.80(1H, d, J=4.0 Hz, H-1)
24b	354	1744 (C=O)	$CDCl_3$: 1.2—2.0(20H, m, CH_2 of cyclohexane rings), 2.08 (3H, s, CH_3), 3.34(1H, br s, CH of cyclohexane ring), 3.98(1H, d, J=2.8 Hz, H-3), 4.45(1H, d, J= 3.8 Hz, H-2), 5.93(1H, d, J=3.8 Hz, H-1)

a) M^+-CH_3. b) KBr.

centrated. The crude product was purified by silica-gel column chromatography using a given solvent system.

3,5-Di-O-acetyl-6-O-(cyclohex-1-enyl)-1,2-O-cyclohexylidene-α-D-glucofuranose (7). A powdered sugar derivative (**1**,[4] 340 mg, 1 mmol) was stirred into a solution of MeMgI (8 mmol) in benzene (15 ml)–ether (10 ml) under a dry nitrogen atmosphere, after which the mixture was heated at 80—85 °C (bath temperature) for 35 min to remove the ether. After the mixture had been cooled, dry pyridine (0.2 ml) was added, followed by the addition of aqueous ammonium chloride. The mixture was then extracted with ether. The extract was washed with water, dried ($MgSO_4$), and concentrated below 35 °C *in vacuo*. The water was removed by co-evaporation with benzene below 35 °C *in vacuo*. The residue was then taken up in dry pyridine (5 ml) and cooled to about 5 °C. To this cold solution, we added acetic anhydride (1.5 ml), after which the mixture was stirred at room temperature for 6 h. After the usual work-up, the mixture was extracted with ether. The extract was washed with water, dried ($MgSO_4$), and concentrated. The pyridine was removed by co-evaporation with xylene. The residue was chromatographed on a silica-gel column with benzene–ethyl acetate (9:1) to give **7** (370 mg, 87%).

3,5-Di-O-acetyl-6-O-cyclohexyl-1,2-O-cyclohexylidene-α-D-glucofuranose (10). *From* ***9***: Acetic anhydride (0.3 ml) was added to a cold (0—5 °C) solution of **9** (95 mg, 0.28 mmol) in dry pyridine (1 ml), and the mixture was stirred at room temperature overnight. The usual work-up gave a crude product, which was chromatographed on a silica-gel column with benzene–ethyl acetate (9:1) to give **10** (112 mg, 95%) as crystals.

From ***7***: The sugar derivative (**7**, 130 mg, 0.3 mmol) was hydrogenated in methanol (20 ml) in the presence of 10% Pd on charcoal (80 mg) with a Parr apparatus at 2.8 kg/cm^2 at room temperature for 7 h. The catalyst was removed by filtration through a Celite pad and washed with methanol. The combined filtrate and washings were concentrated below 35 °C. The residue was chromatographed on a silica-gel column with benzene–ethyl acetate (95:5) to give **10** (80 mg, 61%) as crystals. The physical properties (mp, IR, MS,

Table 3. The physical properties and elemental analyses of the products

Compound	Mp °C	$[\alpha]_D$ (c, $CHCl_3$)	Temp/°C	Formula	Found (%) C	Found (%) H	Calcd (%) C	Calcd (%) H
3	92—93[a]	+1.1° (1.0)	22	$C_{19}H_{32}O_6$	63.90	8.92	64.02	9.05
4	syrup	−1.4° (1.0)	21	$C_{20}H_{34}O_6$	64.92	9.31	64.84	9.25
5	78—80[b]	+33.2° (1.0)	22	$C_{19}H_{32}O_6$	64.06	8.97	64.02	9.05
7	syrup	+0.5° (2.2)	24	$C_{22}H_{32}O_8$	62.31	7.61	62.25	7.60
8	122—124[c]	+41.8° (1.1)	24	$C_{18}H_{28}O_6$	63.57	8.18	63.51	8.29
9	syrup	−5.1° (0.95)[e]	21	$C_{18}H_{30}O_6$	63.14	8.83	63.13	8.83
10	79—81	+6.6° (1.2)	25	$C_{22}H_{34}O_8$	61.93	8.01	61.95	8.04
11	93.0—94.5[d]	+37.3° (0.8)	24	$C_{18}H_{30}O_6$	63.18	8.85	63.13	8.83
12	syrup	−2.2° (0.9)	21	$C_{21}H_{36}O_6$	65.70	9.43	65.59	9.44
15	79—80[b]	−6.4° (1.0)	22	$C_{13}H_{24}O_6$	56.40	8.50	56.50	8.76
16	80.5—81.5[a]	+30.7° (1.0)	22	$C_{13}H_{24}O_6$	56.51	8.66	56.50	8.76
19	syrup	−66.5° (1.1)	23	$C_{15}H_{28}O_5$	62.51	9.61	62.47	9.79
20	syrup	+67.3° (1.2)	18	$C_{15}H_{28}O_5$	62.50	9.76	62.47	9.79
22	syrup	−10.5° (0.3)	20	$C_{18}H_{30}O_5$	66.25	9.20	66.23	9.26
23b	syrup	−12.3° (0.95)	23	$C_{19}H_{28}O_6$	64.63	7.85	64.75	8.01
24a	syrup	−31.7° (1.2)	25	$C_{17}H_{28}O_5$	65.35	9.18	65.36	9.03
24b	syrup	−17.6° (1.0)	23	$C_{19}H_{30}O_6$	64.60	8.52	64.38	8.53

a) Recrystallization from hexane. b) Diisopropyl ether. c) Benzene. d) Benzene–hexane. e) The solvent was ethanol: lit, Ref. 5, $[\alpha]_D^{25}$ −3.7° (c 0.5, EtOH).

and ^1H NMR) of this product were identical with those of the sample prepared from **9**.

*5-O-Acetyl-3-O-(cyclohex-1-enyl)-1,2-O-cyclohexylidene-α-D-xylofuranose (**23b**).* Acetic anhydride (0.3 ml) was added to a cold (0—5 °C) solution of **23a** (140 mg, 0.45 mmol) in dry pyridine (2 ml), and the mixture was stirred at room temperature for 4 h. The usual work-up gave a syrup, which was subsequently chromatographed on a silica-gel column with benzene–ethyl acetate (95:5) to give **23b** (147 mg, 93%) as a syrup.

*5-O-Acetyl-3-O-cyclohexyl-1,2-O-cyclohexylidene-α-D-xylofuranose (**24b**).* *From **24a***: Acetic anhydride (0.3 ml) was added to a cold (0—5 °C) solution of **24a** (220 mg, 0.71 mmol) in dry pyridine (2 ml), after which the mixture was allowed to stand at room temperature overnight. The usual work-up gave a syrup, which was subsequently chromatographed on a silica-gel column with benzene–ethyl acetate (95:5) to give **24b** (245 mg, 95%) as a syrup.

*From **23b***: The sugar derivative (**23b**, 50 mg, 0.14 mmol) was hydrogenated with a Parr apparatus at 3 kg/cm² in methanol (15 ml) in the presence of 10% Pd on charcoal (95 mg) at room temperature for 7 h. The catalyst was removed by filtration through a Celite pad, and washed with methanol. The combined filtrate and washing were concentrated below 35 °C *in vacuo*, and the residue was chromatographed on a silica-gel column with benzene–ethyl acetate (98:2) to afford **24b** (36 mg, 72%) as a syrup. The physical properties (IR and ^1H NMR) of this product was identical with those of the sample prepared from **24a**.

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