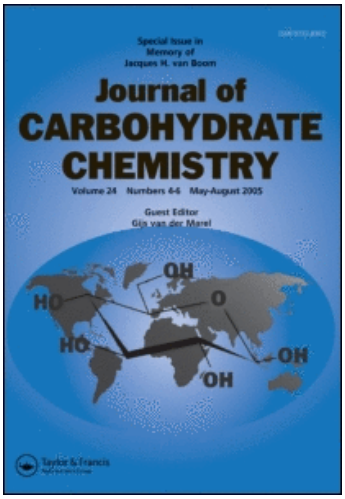

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HYDROGENOLYSIS OF DIOXOLANE-TYPE DIPHENYLMETHYLENE ACETALS BY $AlClH_2$ TO AXIAL DIPHENYLMETHYL ETHERS

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ABSTRACT

A series of dioxolane-type diphenylmethylene acetals of pyranosides was converted into axial diphenylmethyl ethers in high yield using $AlClH_2$ as the reducing agent. AlH_3 did not cleave the acetals, $AlCl_2H$ regenerated both hydroxyl groups, and the intermediate diphenylmethyl ethers were also the substrates of this reagent.

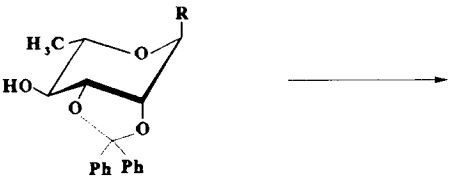
INTRODUCTION

It was found[1] that the hydrogenolysis of dioxolane-type benzylidene derivatives is a highly stereoselective reaction and that the direction of ring cleavage is determined by the orientation of the phenyl group. It was recognized[2] that the *exo*-isomers yielded *axial* hydroxyl/*equatorial* *O*-benzyl derivatives, whereas the

endo-isomers gave *equatorial* hydroxyl/*axial* *O*-benzyl derivatives. Hydrogenolysis of various methylene, isopropylidene and both isomers of acetophenone acetals gave *axial* ethers.[3] However, the methyl and isopropyl ethers are extremely stable under the conditions of hydrogenolysis and, therefore, not suitable for conversions on a preparative scale; the acetophenone derivatives give diastereomeric mixtures of the 2-(1-phenylethyl) ethers. In this study, we demonstrate that the dioxolane-type diphenylmethylene acetals of pyranosides follow the pattern observed in the case of ketals, and give axial diphenylmethyl ethers.[4-5] Some diphenylmethyl ethers were prepared earlier using diazo-(diphenyl)methane[6]-tin(II) chloride reagent.

RESULTS AND DISCUSSION

The known methyl 2,3-*O*-diphenylmethylene- (**1**), methyl 2,3-*O*-diphenylmethylene-1-thio-α-L-rhamnopyranoside (**2**) and some newly prepared compounds (**4-8,10**) were chosen as substrates for the mixed-hydride-type ring-opening reactions. These acetals were prepared as follows: phenyl 1-thio-α-L-rhamnopyranoside (**3**) (obtained by the deacetylation of phenyl 2,3,4-tri-*O*-acetyl-1-thio-α-L-rhamnopyranoside[9]), ethyl 1-thio-α-L-rhamnopyranoside,[10-11] benzyl α-L-rhamnopyranoside,[12] benzyl β-D-arabinopyranoside,[13] and 1,6-anhydro-β-D-mannopyranose[14] were each treated with dichlorodiphenylmethane in pyridine, to give phenyl 2,3-*O*-diphenylmethylene-1-thio-α-L-rhamnopyranoside (**4**), ethyl 2,3-*O*-diphenylmethylene-1-thio- (**5**), benzyl 2,3-*O*-diphenylmethylene-α-L-rhamnopyranoside (**6**), benzyl 3,4-*O*-diphenylmethylene-β-D-arabinopyranoside (**7**) and 1,6-anhydro-2,3-*O*-diphenylmethylene-β-D-mannopyranose (**8**), respectively. Compound **1** was oxidized with pyridinium chlorochromate[15] to give the ulose derivative (**9**) which was reduced by $NaBH_4$ to afford methyl 6-deoxy-2,3-*O*-diphenylmethylene-α-L-talopyranoside (**10**). To open the diphenylmethylene acetal rings, the following reagents were tested: AlH_3,[16] $AlClH_2$,[16] $AlCl_2H$,[16] $NaCN{\cdot}BH_3$-HCl[17] and $(CH_3)_3N{\cdot}BH_3$-$AlCl_3$[18] in boiling ether-dichloromethane (1:1). The alane (AlH_3) did not react with these acetals. On the other hand, the dichloroalane ($AlCl_2H$), $NaCN{\cdot}BH_3$-HCl and $(CH_3)_3N{\cdot}BH_3$-$AlCl_3$ cleaved the acetal rings completely, thus regenerating the diols. However, treatment of acetals **1,2,4-6,10** with chloroalane ($AlClH_2$) were single-product reactions yielding **11-16**. These ethers proved to be *axial* ethers (periodate oxidation and ^{13}C NMR spectroscopy). Each L-rhamnopyranoside and 6-deoxy-L-talopyranoside ether could be oxidized with periodate and therefore contained vicinal hydroxyl groups.



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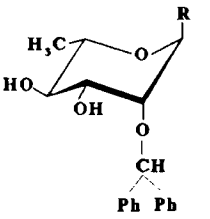
4 R= SPh
5 R= SCH_2- CH_3
6 R= OBzl



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13 R= SPh
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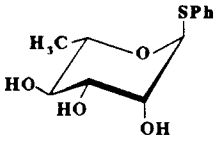

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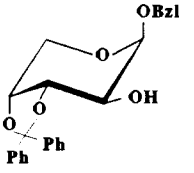

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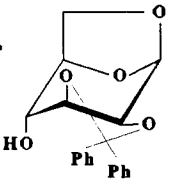

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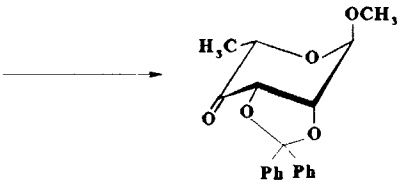
1 

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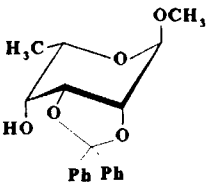

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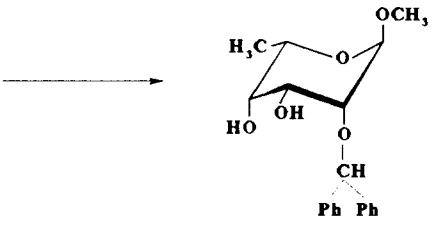
10 

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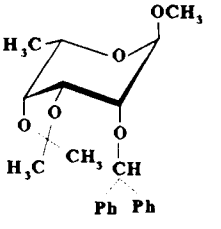

17

The ^{13}C NMR spectra showed that the diphenylmethyl moiety caused an ~ +6 ppm α-shift, and a large negative β-shift in the pyranosyl skeleton. The β-shift effects on the resonance of C-1 are especially strong (up to ~ -2 ppm for the 2-ethers).

Under the applied reaction conditions compounds **7** and **8** were not converted into ethers. The arabinopyranoside derivative **7** did not react with $AlClH_2$, whereas in the case of **8** the starting compound (1,6-anhydro-β-D-manno-pyranose) was regenerated. Generally, the diphenylmethylene acetals show properties similar to those observed with fluoren-9-ylidene acetals.[19]

The diphenylmethyl group is readily hydrogenolysed over a palladium-on-carbon catalyst. Treatment of these ethers (**11,12,14-16**) with sodium in ethanol gave the corresponding methyl α-L-, methyl 1-thio-α-L-, ethyl 1-thio-α-L-, benzyl α-L-rhamnopyranoside and methyl 6-deoxy-α-L-talopyranoside.

Although the diphenylmethyl ethers are acid-labile, they are sufficiently stable to allow selective removal of acetal groups by acid hydrolysis. Thus, compound **16** was treated with 2,2-dimethoxypropane in the presence of *p*-toluene-sulfonic acid to give methyl 6-deoxy-2-*O*-diphenymethyl-3,4-*O*-isopropylidene-α-L-talopyranoside (**17**). Compound **17** was heated with aqueous acetic acid to give methyl 6-deoxy-2-*O*-diphenylmethyl-α-L-talopyranoside (**16**). The diphenylmethyl ethers are stable under basic conditions, but they can be removed by hydrogenolysis with either $AlCl_2H$ or $(CH_3)_3N{\cdot}BH_3$-$AlCl_3$. Under these conditions the allyl and benzyl ethers are stable. Owing to these properties the diphenylmethyl ether group may be a useful protecting group in carbohydrate chemistry.

EXPERIMENTAL

General methods. Solutions were concentrated at 40 °C (bath) under diminished pressure. Optical rotations were measured at room temperature with a Perkin-Elmer 241 automatic polarimeter. The ^1H (200 and 400 MHz) and ^{13}C NMR (50.3 MHz) spectra for solutions in $CDCl_3$ were recorded with a Bruker WP-200 SY and Varian XLA-400 spectrometers (internal Me_4Si). Heteronuclear correlation spectroscopy was used to assign lines in the ^{13}C NMR spectra. Melting points were determined on a Kofler apparatus and are uncorrected. TLC was performed on Kieselgel 60 F_{254} (Merck) with A (95:5) B (9:1) C (8:2) dichloromethane-acetone, and D (9:1) E (8:2) hexane-ethyl acetate, with detection by spraying with sulfuric acid followed by heating.

Preparation of diphenylmethylene acetals (1,2,4-8). To a solution of the substrate in dry pyridine (15 mL/g), was added dichlorodiphenylmethane (2 equiv). The mixture was stirred for 4 days at 110 °C (TLC solvent A or B). The dark-red solution was poured onto crushed ice and, after 1 h, the mixture was partitioned between dichloromethane and 0.5M sulfuric acid. The organic phase was washed with water until neutral, dried (Na_2SO_4), and concentrated. The dark-red residue was passed through a short column of silica gel (solvent A). The appropriate fractions were combined and concentrated, to give the product (51-67%).

Phenyl 2,3-*O*-Diphenylmethylene-1-thio-α-L-rhamnopyranoside (4). Column chromatography (solvent E) of the crude product gave amorphous **4** (58%), $[\alpha]_D^{20}$ -164.1° (*c* 1.02, chloroform), R_F 0.38 (solvent E).

Anal. Calcd for $C_{25}H_{24}O_4S$ (420.52): C, 71.41; H, 5.75. Found: C, 71.45; H, 5.74.

Ethyl 2,3-*O*-Diphenylmethylene-1-thio-α-L-rhamnopyranoside (5). Compound **5**, (67%), had mp 99-100 °C (from cyclohexane), $[\alpha]_D^{20}$ -188.3° (*c* 0.52, chloroform), R_F 0.63 (solvent A).

Anal. Calcd for $C_{21}H_{24}O_4S$ (372.48): C, 67.72; H, 6.49. Found: C, 67.80; H, 6.51.

Benzyl 2,3-*O*-Diphenylmethylene-α-L-rhamnopyranoside (6). Compound **6**, (59%), had mp 104-105 °C (from cyclohexane), $[\alpha]_D^{20}$ -102.8° (*c* 0.52, chloroform), R_F 0.54 (solvent A).

Anal. Calcd for $C_{26}H_{26}O_5$ (418.49): C, 74.62; H, 6.26. Found: C, 74.58; H, 6.25.

Benzyl 3,4-*O*-Diphenylmethylene-β-D-arabinopyranoside (7). Column chromatography (solvent A) of the crude product gave amorphous **7**, (51%), $[\alpha]_D^{20}$ -70.5° (*c* 0.59, chloroform), R_F 0.63 (solvent A).

Anal. Calcd for $C_{25}H_{24}O_5$ (404.46): C, 74.24; H, 5.98. Found: C, 74.19; H, 5.96.

1,6-Anhydro-2,3-*O*-diphenylmethylene-β-D-mannopyranose (8). Compound **8**, (73%), had mp 218-219 °C (from ethanol), $[\alpha]_D^{20}$ -77.7° (*c* 0.47, chloroform), R_F 0.54 (solvent B).

Anal. Calcd for $C_{19}H_{18}O_5$ (326.35): C, 69.93; H, 5.56. Found: C, 69.90; H, 5.58.

Methyl 6-Deoxy-2,3-*O*-diphenylmethylene-α-L-talopyranoside (10). To a solution of **1** (500 mg, 1.46 mmol) in dry dichloromethane (15 mL), 4 Å molecular sieves (500 mg) and pyridinium chlorochromate (2.5 g) were added. The mixture was stirred in the dark, at room temperature, overnight, filtered through a short column of silica gel (solvent E), and concentrated. The yellow residue (**9**, 460 mg,

93%) was used for the next step without any purification. To a solution of **9** (400 mg) in methanol (10 mL), $NaBH_4$ (90 mg, 2 equiv) was added, and the solution was stirred for 2 h at room temperature. The excess of $NaBH_4$ was decomposed with aqueous acetic acid, and the mixture was concentrated. Column chromatography (solvent A) of the residue gave amorphous **10** (345 mg, 86% from **9**), R_F 0.72 (solvent D), $[\alpha]_D^{20}$ -94.5° (*c* 1.04, chloroform).

Anal. Calcd for $C_{20}H_{22}O_5$ (342.39): C, 70.16; H, 6.48. Found: C, 70.13; H, 6.50.

Preparation of the axial diphenylmethyl ethers (11-16). To a solution (100mg/10mL) of the diphenylmethylene acetal in dry 1:1 dichloromethane-ether was added $LiAlH_4$ (2 equiv/1 equiv of substrate) and $AlCl_3$ (2 equiv/1 equiv of substrate). The solution was heated under reflux and the reaction was monitored by TLC (solvent A). When the conversion of the starting material was complete (10-40 min) the mixture was diluted with ether, the excess of $LiAlH_4$ was decomposed by successive addition of ethyl acetate and water, the organic layer was washed twice with water, dried (Na_2SO_4), and concentrated. The yields were quantitative.

Methyl 2-*O*-Diphenylmethyl-α-L-rhamnopyranoside (11). Prepared from **1**, compound **11** had mp 102-103 °C (from *n*-hexane-ethyl acetate), $[\alpha]_D^{20}$ +31.0° (*c* 0.34, chloroform), R_F 0.48 (solvent C).

Anal. Calcd for $C_{20}H_{24}O_5$ (344.41): C, 69.75; H, 7.02. Found: C, 69.79; H, 7.00.

Methyl 2-*O*-Diphenylmethyl-1-thio-α-L-rhamnopyranoside (12). Prepared from **2**, column chromatography (solvent A) of the crude product gave amorphous **12** (90%), $[\alpha]_D^{20}$ -12.7° (*c* 0.64, chloroform), R_F 0.34 (solvent A).

Anal. Calcd for $C_{20}H_{24}O_4S$ (360.47): C, 66.64; H, 6.71. Found: C, 66.66; H, 6.70.

Phenyl 2-*O*-Diphenylmethyl-1-thio-α-L-rhamnopyranoside (13). Prepared from **4**, column chromatography (solvent A) of the crude product gave amorphous **13** (92%), $[\alpha]_D^{20}$ -13.1° (*c* 0.92, chloroform), R_F 0.28 (solvent A).

Anal. Calcd for $C_{25}H_{26}O_4S$ (422.54): C, 71.06; H, 6.20. Found: C, 71.09; H, 6.19.

Ethyl 2-*O*-Diphenylmethyl-1-thio-α-L-rhamnopyranoside (14). Prepared from **5**, column chromatography (solvent A) of the crude product gave amorphous **14** (95%), $[\alpha]_D^{20}$ -28.3° (*c* 0.78, chloroform), R_F 0.39 (solvent A).

Anal. Calcd for $C_{21}H_{26}O_4S$ (374.49): C, 67.35; H, 7.00. Found: C, 67.40; H, 7.02.

TABLE I. ^{13}C NMR chemical shifts (ppm)

Comp.	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*C-9'*	*Other signals*
1	98.05	77.00	79.03	75.94	65.88	17.41	109.54	54.86, OCH_3
2	81.00	76.97	79.05	74.72	66.02	17.25	109.48	13.26, SCH_3
3	87.89	72.59	72.75	74.87	69.40	17.51	-	-
4	83.62	76.99	79.12	74.60	66.99	17.00	109.61	-
5	79.42	77.17	79.09	74.78	66.08	17.19	109.48	14.61, SCH_2-$\underline{C}H_3$
								24.48, $S\underline{C}H_2$-CH_3
6	96.31	76.02	78.96	73.90	66.21	17.45	109.53	69.28, $O\underline{C}H_2$-Ph
7	96.68	69.26	76.33	73.36	59.81	-	109.62	69.69, $O\underline{C}H_2$-Ph
8	99.19	71.85	76.41	69.71	75.76	64.37	110.17	-
10	98.22	73.11	73.52	66.42	64.12	16.73	109.58	55.02, OCH_3
11	98.45	76.98	71.56	74.15	67.58	17.66	83.79	54.69, OCH_3
12	82.90	78.24	72.03	74.47	68.26	17.64	83.11	13.62, SCH_3
13	85.58	78.30	71.99	74.37	69.31	17.55	83.16	-
14	81.49	78.61	71.99	74.38	68.30	17.57	83.26	14.83, SCH_2-$\underline{C}H_3$
								25.11, $S\underline{C}H_2$-CH_3
15	96.63	76.99	71.67	74.26	68.07	17.67	83.77	68.90, $O\underline{C}H_2$-Ph
16	102.23	79.19	70.91	67.29	65.82	17.22	86.12	55.07, OCH_3
17	101.83	75.15	73.82	77.34	65.69	15.45	83.32	25.30, 26.28, $C(\underline{C}H_3)_2$
								55.08, OCH_3,
								110.20, $\underline{C}(CH_3)_2$

Benzyl 2-*O*-Diphenylmethyl-α-L-rhamnopyranoside (15). Prepared from **6**, column chromatography (solvent A) of the crude product gave amorphous **15** (94%), $[\alpha]_D^{20}$ -16.5° (*c* 0.59, chloroform), R_F 0.35 (solvent A).

Anal. Calcd for $C_{26}H_{28}O_5$ (420.50): C, 74.26; H, 6.71. Found: C, 74.23; H, 6.75.

Methyl 6-Deoxy-2-*O*-diphenylmethyl-α-L-talopyranoside (16). Prepared from **10**, compound **16** had mp 91-93 °C (from ethanol), $[\alpha]_D^{20}$ -61.3° (*c* 0.11, chloroform), R_F 0.42 (solvent A).

Anal. Calcd for $C_{20}H_{24}O_5$ (344.41): C, 69.75; H, 7.02. Found: C, 69.73; H, 7.00.

Methyl 6-Deoxy-2-*O*-diphenylmethyl-3,4-*O*-isopropylidene-α-L-talopyranoside (17). To a solution of **16** (344 mg, 1.0 mmol) in 2,2-dimethoxypropane (2 mL, 16 mmol) was added a catalytic amount of *p*-toluenesulfonic acid and the mixture was

TABLE II. ^{1}H NMR chemical shifts (ppm)

Comp.	*H-1*	*H-2*	*H-3*	*H-4*	*H-5*	*H-6*	*H-9'*	*Other signals*
1	5.02 (s)	4.05 (d)	4.28 (t)	3.41 (dd)	3.69 (m)	1.27 (d)	-	3.38, OCH_3 (s)
2	5.55 (s)	4.10 (d)	4.27 (t)	3.41 (dd)	3.95 (m)	1.25 (d)	-	2.11, SCH_3 (s)
3	5.49 (d)	4.25 (dd)	3.83 (dd)	3.59 (t)	4.16 (m)	1.31 (d)	-	-
4	5.90 (s)	4.27 (d)	4.33 (t)	3.41 (dd)	4.09 (m)	1.16 (d)	-	-
5	5.70 (s)	4.10 (d)	4.28 (dd)	3.40 (dd)	4.00 (m)	1.24 (d)	-	1.30, SCH_2-C$\underline{H}_3$ (t)
								2.60, S$\underline{CH}_2$-CH_3 (dd)
6	5.22 (s)	4.10 (d)	4.32 (t)	3.40 (t)	3.77 (m)	1.25 (d)	-	4.61, O$\underline{CH}_2$-Ph (dd)
7	4.92 (d)	3.83 (m)	--------	4.10 - 4.39 (m)	--------	-	-	4.67, O$\underline{CH}_2$-Ph (dd)
8	5.51 (d)	4.20 (dd)	4.02 (m)	4.10 (d)	4.56 (m)	-	-	3.79, H_a-6 (dd)
								4.06, H_b-6 (dd)
10	5.13 (d)	3.83 (dd)	4.39 (dd)	3.65 (t)	3.83 (m)	1.33 (d)	-	3.38, OCH_3 (s)
11	4.58 (d)	3.79 (dd)	3.68 (dd)	3.53 (t)	3.60 (m)	1.35 (d)	5.54 (s)	3.26, OCH_3 (s)
12	5.14 (s)	3.89 (dd)	3.67 (m)	3.58 (t)	3.93 (m)	1.36 (d)	5.53 (s)	2.03, SCH_3 (s)
13	5.42 (s)	4.05 (d)	3.72 (m)	3.62 (t)	4.09 (m)	1.35 (d)	5.51 (s)	-
14	5.18 (s)	3.89 (d)	3.68 (dd)	3.57 (t)	3.96 (m)	1.33 (d)	5.53 (s)	1.16, SCH_2-C$\underline{H}_3$ (t)
								2.49, S$\underline{CH}_2$-CH_3 (dd)
15	4.77 (s)	----------	3.51 - 3.85 (m)	----------		1.36 (d)	5.49 (s)	4.51, O$\underline{CH}_2$-Ph (dd)
16	4.80 (s)	----------	3.46 - 3.83 (m)	----------		1.09 (d)	5.75 (s)	3.36, OCH_3 (s)
17	4.85 (d)	3.54 (dd)	4.43 (dd)	3.95 (dd)	3.62 (m)	1.17 (d)	5.80 (s)	1.34, 1.51, $C(CH_3)_2$ (s)
								3.42, OCH_3 (s)

stirred overnight at room temperature. The reaction mixture was diluted with dichloromethane, washed with water until neutral, dried (Na_2SO_4), and concentrated. The crude product was purified by column chromatography (solvent A), to give amorphous **17** (62%), $[\alpha]_D^{20}$ -12.55° (*c* 0.86, chloroform), R_F 0.42 (solvent A).

Anal. Calcd for $C_{23}H_{28}O_5$ (384.47): C, 71.85; H, 7.34. Found: C, 71.81; H, 7.37.

Removal of the isopropylidene group in 17. To compound **17** (384 mg, 1.0 mmol) was added 5 mL 40% aqueous acetic acid and the solution was stirred at 60 °C. After 2 h TLC (solvent A) indicated complete reaction, the only product was compound **16**.

Removal of the diphenylmethyl group in 11 by catalytic hydrogenolysis. To a solution of **11** (300 mg, 0.87 mmol) in ethanol (30 mL), 10 % Pd/C (30 mg) and 3

drops of acetic acid were added and the mixture was stirred under H_2. After 12 h, the only product (TLC) was methyl α-L-rhamnopyranoside (140 mg, 90%).

Removal of the diphenylmethyl group in 11 by hydrogenolysis with $AlCl_2H$. To a solution of **11**, (100 mg, 0.29 mmol) in dry 1:1 dichloromethane-ether (10 mL), $LiAlH_4$ (34 mg, 3 equiv) and $AlCl_3$ (350 mg, 9 equiv) was added, and the mixture was heated under reflux. After 2 h, TLC (solvent A) indicated complete reaction. The mixture was diluted with ether, the excess of $LiAlH_4$ was decomposed by successive addition of ethyl acetate and water, the organic layer was concentrated, and crystallization from ethyl acetate gave methyl α-L-rhamnopyranoside (40 mg, 74%).

Removal of the diphenylmethyl group in 11 with sodium in ethanol. To a solution of **11**, (100 mg, 0.29 mmol) in dry ethanol (5 mL), Na (115 mg, 5 equiv) was added, and the mixture was stirred at room temperature. After 2 days, the only product (TLC) was methyl α-L-rhamnopyranoside.

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