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Note

A new route to *C*-glycosyl compounds. Wittig-type reaction promoted by zinc

Lydie Dheilly, Catherine Fréchou*, Daniel Beaupère, Raoul Uzan, and Gilles Demailly
Laboratoire de Chimie Organique, Faculté des Sciences, Université D'Amiens, 33, Rue Saint Leu, F-80039 Amiens (France)

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In recent years, methods for the preparation of *C*-glycosyl compounds have become increasingly important in synthetic organic chemistry. These compounds are useful as subunits for the synthesis of biological active products[1] and as potential enzyme inhibitors[2]. Significant attention has been focused on the development of new routes to prepare functionalized *C*-glycosyl compounds that are synthetic precursors of more complex *C*-glycosyl compounds. The starting materials can be furanose or pyranose carbohydrates, the main problem being the stereoselective introduction of a functionalized carbon atom at C-1.

A widely used procedure to obtain carbon–carbon bonding at the anomeric position of carbohydrates was first reported by Zhdanov *et al.*[3] This two-step procedure involves the formation of an unsaturated, open-chain intermediate, followed by a cyclization leading to the expected *C*-glycosyl compound. The first step is a Wittig reaction with protected furanose and pyranose hemiacetals. When stabilized ylides are used[4], subsequent cyclization of the unsaturated intermediate may occur by treatment with bases or, sometimes, spontaneously. But when the Wittig reaction takes place with unstabilized ylides, the cyclization can be obtained by the iodo- or mercuro-cyclization process[5]. It should be noted that *C*-glycosyl compounds can be synthesized in the same way when phosphonates are used instead of phosphoranes[6]. Lastly, although stereoselective routes exist for both *C*-α- and β-glycosyl compounds, they mainly lack a general application. Stereoselectivity indeed depends on carbohydrate structures, ylides, and solvents. In the case of 2,3,4,6-tetra-*O*-benzyl-α,β-D-glucopyranose (1), Nicotra *et al.*[7] have observed an abnormal reaction of (carbethoxymethylene)triphenylphosphorane leading solely to a diene. The same elimination by Wittig reaction was observed for 3,4,6-tri-*O*-acetyl-2-*O*-benzyl-α,β-D-glucopyranose and partial elimination for 2,3,4,6-tetra-*O*-acetyl-α,β-D-glucopyranose. These abnormal reactions led Allevi *et al.*[6] to use a Wittig–Horner reaction with **1** and sodium triethylphosphonoacetate

* To whom correspondence should be addressed.

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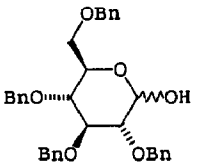
to obtain the corresponding α- and β-D-glucopyranosylacetates with a yield of 77% and a ratio of α to β of 2.3:1; however, a partial epimerization at C-2 was also observed, leading to some D-mannopyranosylacetates (9%). Moreover, this reaction is very sensitive to experimental conditions and Monti *et al.*[8] have reported high yields of epimerization at lower temperature, with the main product of the Wittig–Horner reaction with **1** being the *C*-mannopyranosyl compound.

A new method by Shen *et al.*[9] for the transformation of an aromatic or aliphatic aldehyde into a functionalized olefin has been described, and we report herein the



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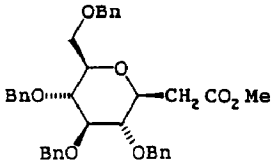

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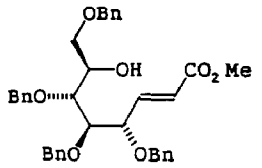

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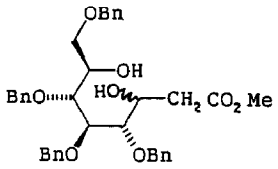

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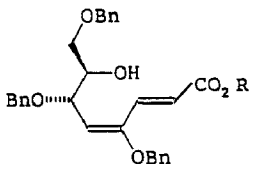
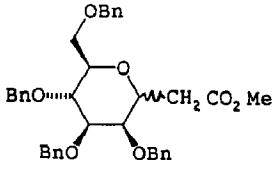


5 R = Me
6 R = Bn



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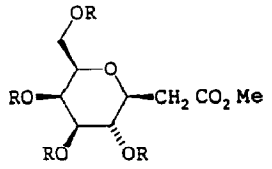

8 R = Bn
9 R = Ac

application of this one-pot reaction to glycopyranoses. Heating **1** in refluxing benzene with tributylphosphine, zinc dust, and methyl bromoacetate gave solely the *C*-β-D-glucopyranosyl compound[6] **2** in a yield of 64%, without traces of *C*-α-D-glucopyranoside nor *C*-D-mannopyranosides. Monitoring of the reaction by t.l.c., however, indicated the formation of an intermediate, more polar than **2**, which could be isolated when the reaction was stopped when some **1** was still present and **2** began to appear. N.m.r. spectroscopy indicated the structure of the *trans*-2,3-unsaturated ester **3** (^{13}C-n.m.r: two ethylenic methine groups at δ 122.22 and 145.58; ^{1}H-n.m.r.: two ethylenic protons at δ 6.13 and 7.08 with a coupling constant of 15.8 Hz).The stereoselective cyclization of **3** spontaneously occurs in refluxing benzene to give **2**. Anomerization of *C*-α- to -β-D-glucopyranosyl compounds has been reported under mild basic conditions[10]. Since no formation of the α-D anomer was detected during the cyclization of **3**, we assume that anomerization was not responsible for the selectivity.

To further our understanding of this reaction mechanism, additional experiments were performed. Firstly, the same reaction with **1** was conducted without tributylphosphine, under the conditions of the Reformatsky reaction. Various investigators have reported Reformatsky reactions only with uloses[11], lactones[12], or a fully protected *aldehydo*-D-mannose[13]. The reaction of **1** with methyl bromoacetate and zinc in refluxing benzene gave in 60% yield, the 3-hydroxyesters **4** (1:1 mixture of separable diastereoisomers) which are the expected Reformatsky products. These 3-hydroxyesters **4** were not dehydrated by subsequent addition of tributylphosphine and, therefore, the *C*-glycosylation described herein is not a Reformatsky-type reaction.

In another experiment, quantitative formation of a phosphonium salt is obtained when tributylphosphine and methyl bromoacetate are heated in refluxing benzene. Without zinc, this phosphonium salt did not react with **1** but, as soon as zinc was added, the color of the reaction mixture turned to orange, and formation of the intermediate olefin **3** was detected, followed by the formation of **2**, suggesting a Wittig-type reaction. A Wittig reaction on **1** was performed with the same ylide generated by use of butyllithium and the elimination products **5** and **6** were mainly obtained, **6** resulting from transesterification of **5** with eliminated benzyl alcohol; this result is similar to that reported by Nicotra *et al.*[7]

The reaction of methyl bromoacetate, tributylphosphine, and zinc was extended to other glycopyranoses. 2,3,4,6-Tetra-*O*-benzyl-α,β-D-mannopyranose[14] gave the *C*-D-mannopyranosyl compound[6] **7** (1:1 mixture of anomers) in 49% yield, and 2,3,4,6-tetra-*O*-benzyl-D-galactopyranose[14] gave only the *C*-β-D-galactopyranosyl compound **8** in 75% yield. The β orientation at C-1 was established by n.m.r. spectroscopy of the corresponding tetra-*O*-acetyl derivative **9**. Thus, the same stereospecificity was observed with D-glucose and D-galactose derivatives, but no stereoselectivity with the D-mannose derivative.

In summary, the reaction of aldoses with tributylphosphine, methyl bromoacetate, and zinc leads to *C*-glycosyl compounds by involving a Wittig-type reaction; in the case of **1** the *C*-β-D-glucosyl compound is stereospecifically obtained. This reaction is a new interesting route to *C*-glycosyl compounds.

EXPERIMENTAL

General. — Melting points were determined with a Büchi apparatus and are uncorrected. Optical rotations were measured with a Jobin–Yvon polarimeter. T.l.c. was performed on Silica Gel 60F-254 Merck (230 mesh). Column chromatography was performed on Silica gel 35–70 μm (400–200 mesh) Amicon. The ^{1}H- and ^{13}C-n.m.r. spectra were recorded with a Bruker WB 300 spectrometer. Elemental analyses were performed by the Laboratoire Central d'Analyses du C.N.R.S. (Vernaison, France).

Methyl 2-(2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyl)acetate (2). — To a solution of commercial 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (**1**; 1 g, 1.85 mmol) and acid-washed Zn dust[15] (2.4 g, 37 mmol, 20 equiv.) in anhydrous benzene (8 mL) were added, at room temperature, tributylphosphine (2.3 mL, 9.26 mmol, 5 equiv.) and

methyl bromoacetate (0.87 mL, 9.26 mmol, 5 equiv.). The mixture was heated at reflux and the reaction monitored by t.l.c. (4:1 hexane–EtOAc). After 20 h, the mixture was concentrated and chromatographic purification on silica gel (4:1 hexane–EtOAc) afforded **2** (64% yield), m.p. 66–68° (lit.[6] 65–66°), $[\alpha]_D^{20}$ −0.7° (*c* 1, $CHCl_3$) {lit.[6] $[\alpha]_D$ −3.5° (*c* 1, $CHCl_3$)}; R_F 0.37 (4:1 hexane–EtOAc); ^{1}H-n.m.r: identical with that reported earlier[6]; ^{13}C-n.m.r ($CDCl_3$): δ 37.42 (C-1′), 51.56 (CH_3), 68.76 (C-6), 73.36, 74.97, 75.48 (4 Ph-CH_2), 75.86, 78.48, 79.17, 81.28, 87.14 (C-1,2,3,4,5), 127.48–128.35 (*C*H(Ph)), 137.96–138.39 (C-*ipso*), and 171.39 (C = O).

*(E)-Methyl 4,5,6,8-tetra-*O*-benzyl-2,3-dideoxy-*D-gluco*-oct-2-enonate* (**3**). — The reaction affording **2** was monitored by t.l.c. After 3 h, some starting material was still present, **2** began to appear, and some intermediate **3** was formed. Chromatographic purification on silica gel in 4:1 hexane–EtOAc afforded **3**, syrup, $[\alpha]_D^{20}$ +10° (*c* 0.4, $CHCl_3$); R_F 0.20 (4:1 hexane–EtOAc); ^{1}H-n.m.r ($CDCl_3$): δ 3.63–3.72 (m, 2 H, H-8a,8b), 3.73 (s, 3 H, Me), 3.78–3.85, 3.90–3.96, 4.06–4.16, 4.32–4.40 (4 m, 4 H, H-4,5,6,7), 4.42–4.85 (4 AB syst, 8 H, 4 PhCH_2), 6.13 (d, 1 H, $J_{2,3}$ 15.8 Hz, H-2), 7.08 (dd, 1 H, $J_{2,3}$ 15.8, $J_{3,4}$ 5.7 Hz, H-3), and 7.20–7.50 (m, 20 H, 4 C_6H_5); ^{13}C-n.m.r. ($CDCl_3$) : δ 51.59 (CH_3), 70.29, 78.09, 78.50, 80.51 (C-4,5,6,7), 71.08, 71.89, 73.25, 73.39, 74.72 (C-8 and 4 Ph-CH_2), 122.22 (C-2), 127.65–128.52 (*C*H(Ph)), 137.71–138.19 (C-*ipso*), 145.58 (C-3), and 166.46 (C = O).

Anal. Calc. for $C_{37}H_{40}O_7$: C, 74.47; H, 6.75. Found: C, 74.20; H 6.99.

*Methyl 2-(2,3,4,6-tetra-*O*-benzyl-α,β-*D*-mannopyranosyl)acetate* (**7**). — This compound was prepared from 2,3,4,6-tetra-*O*-benzyl-α,β-D-mannopyranose [14] according to the procedure given for the preparation of **2**. After 18 h, chromatographic purification on silica gel in 17:3 hexane–EtOAc afforded a 1:1 mixture of the α and β anomers of **7** in 49% yield.

α Anomer. Syrup, R_F 0.33 (4:1 hexane–EtOAc); $[\alpha]_D^{20}$ +8.1° (*c* 1.1, $CHCl_3$) {lit.[6] $[\alpha]^{20}$ +9.7° (*c* 1, $CHCl_3$)}; ^{1}H-n.m.r: identical with that reported earlier[6]; ^{13}C-n.m.r. ($CDCl_3$): δ 36.43 (C-1′), 51.67 (CH_3), 68.57, 74.34, 74.38, 75.21, 75.45 (C-1,2,3,4,5), 68.73 (C-6), 71.23, 72.22, 72.99, 73.29 (4 PH-CH_2), 127.48–128.35 (*C*H(Ph)), 137.96–138.39 (*C*-ipso), and 171.39 (C = O).

β Anomer. Syrup, $[\alpha]_D^{20}$ +8.0° (*c* 1, $CHCl_3$) {lit.[6] $[\alpha]_D$ +8.5° (*c* 1, $CHCl_3$)}; R_F 0.30 (4:1 hexane–EtOAc); H^1-n.m.r: identical with that reported earlier[6]; ^{13}C-n.m.r ($CDCl_3$): δ 36.86 (C-1′), 51.57 (CH_3), 69.43 (C-6), 72.59, 73.34, 74.31, 75.15 (4 Ph-CH_2), 74.39, 74.56, 75.06, 79.78, 85.00 (C-1,2,3,4,5), 127.58–128.43 (*C*H(Ph)), 138.37–138.44 (C-*ipso*), and 171.55 (C = O).

*Methyl 2-(2,3,4,6-tetra-*O*-benzyl-β-*D*-galactopyranosyl)acetate* (**8**). — This compound was prepared from 2,3,4,6-tetra-*O*-benzyl-α,β-D-galactopyranose[14] according to the procedure given for **2**. After 18 h, chromatographic purification on silica gel in 4:1 hexane–EtOAc afforded **8** in 75% yield, syrup, $[\alpha]_D^{20}$ +8.6° (*c* 1.3, $CHCl_3$); R_F 0.36 (4:1 hexane–ethyl acetate); ^{1}H-n.m.r ($CDCl_3$): δ 2.65 (dd, 1 H, $J_{1'a,1'b}$ 15, $J_{1'a,1}$ 7 Hz, H-1′a), 2.92 (dd, 1 H, $J_{1'a,1'b}$ 15, $J_{1'b,1}$ 4 Hz, H-1′b), 3.64 (s, 3 H, Me), 3.66–4.20 (7 H), 4.50–5.20 (4 AB syst, 8 H, 4 Ph-CH_2), and 7.25–7.70 (m, 20 H, 4 C_6H_5); ^{13}C-n.m.r ($CDCl_3$): δ 37.90 (C-1′), 51.61 (*C*H_3), 68.83 (C-6), 72.17, 73.48, 74.76, 75.23 (4 Ph-*C*H_2), 74.06, 76.49, 77.32,

78.30, 84.82 (C-1,2,3,4,5), 127.70–128.52 (*C*H(Ph)), 138.23–138.93 (C-*ipso*), and 171.57 (C = O).

Anal. Calc. for $C_{37}H_{40}O_7$: C, 74.47; H, 6.75. Found: C, 74.57; H, 6.60.

*Methyl 2-(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)acetate* (**9**). — Compound **8** (150 mg), dissolved in MeOH (15 mL), was stirred with Pd–C (350 mg) and ammonium formiate (150 mg) at 70° for 20 h. The solution was filtered and concentrated, and the residue was dissolved in dry pyridine (6 mL) and stirred with acetic anhydride (0.4 mL) at room temperature for 24 h. The mixture was concentrated and chromatographic purification of the residue on silica gel in 5:1 hexane–EtOAc afforded **9** in 95% yield, syrup, ^{1}H-n.m.r ($CDCl_3$): δ 1.95, 2.00, 2.02, 2.12 (4s, 12 H, 4 CH_3), 2.34–2.63 (m, 2 H, H-1'a,1'b), 3.68 (s, 3 H, OCH_3) 3.85–3.95 (m, 2 H, H-1,5), 3.97–4.11 (m, 2 H, H-6a,6b) 5.01 (dd, 1 H, $J_{2,3}$ 10.1, $J_{3,4}$ 3.2 Hz, H-3), 5.07 (dd, 1 H, $J_{1,2}$ 9.7, $J_{2,3}$ 10.1 H, H-2), and 5.40 (dd, 1 H, $J_{3,4}$ 3.2, $J_{4,5}$ 1.0 Hz, H-4); ^{13}C-n.m.r ($CDCl_3$): δ 20.53 (CH_3), 37.26 (C-1'), 51.79 (OCH_3), 61.29 (C-6), 67.55 (C-4), 68.93 (C-2), 71.87 (C-3), 74.22, 74.91 (C-1,5), and 169.74–170.52 (5 C = O).

*Methyl 4,5,6,8-tetra-*O*-benzyl-2-deoxy-*D*-glycero-*D*-gulo- or -*D*-ido-octonate* (**4**). — To a solution of 2,3,4,6-tetra-*O*-benzyl-α,β-D-glucopyranose (**1**; 1 g, 1.85 mmol) and acid-washed Zn dust (2.4 g, 37 mmol, 20 equiv.) in anhydrous benzene (8 mL) was added, at room temperature, methyl bromoacetate (0.87 mL, 9.26 mmol, 5 equiv.). The mixture was heated at reflux and monitored by t.l.c. (elution with 3:2 hexane–EtOAc). After 4 h, the starting sugar had disappeared, and the mixture was concentrated and eluted from a column of silica gel in 4:1 hexane–EtOAc to give **4** (60% yield) in 1:1 ratio.

Less polar diastereoisomer. Syrup, R_F 0.17 (4:1 hexane–EtOAc); ^{1}H-n.m.r ($CDCl_3$): δ 2.50 (dd, 1 H, $J_{2a,3}$ 9.6, $J_{2a,2b}$ 15 Hz, H-2a), 2.66 (dd, 1 H, $J_{2b,3}$ 4.8, $J_{2a,2b}$ 15 Hz, H-2b), 3.62 (s, 3 H, OCH_3), 3.66 (AB part of ABX, 2 H, H-8a,8b), 3.71–3.78, 3.82–3.89, 3.90–3.96, 4.04–4.15, 4.26–4.35 (5 m, 5 H, H-3,4,5,6,7), 4.46–4.65 (4 AB, 8 H, 4 Ph-CH_2), and 7.24–7.45 (m, 20 H, 4 C_6H_5); ^{13}C-n.m.r ($CDCl_3$): δ 38.18 (C-2), 51.64 (OCH_3), 69.31, 70.75 (C-3,7) 71.07 (C-8) 73.45, 73.59, 73.86, 74.19 (4 Ph-*C*H_2), 77.48, 78.78, 79.77 (C-4,5,6), 127.61–128.54 (*C*H(Ph)), 137.56–137.92 (C-*ipso*), and 173.16 (C = O).

More polar diastereoisomer. Syrup, R_F 0.12 (4:1 hexane–EtOAc); ^{1}H-n.m.r ($CDCl_3$): δ 2.21, (dd, 1 H, $J_{2a,3}$ 4.5, $J_{2a,2b}$ 16.0 Hz, H-2a), 2.48 (dd, 1 H, $J_{2b,3}$ 8.5, $J_{2a,2b}$ 16.0 Hz, H-2b), 3.52 (s, 3 H, OCH_3), 3.59 (AB part of ABX, 2 H, H-6a,6b), 3.54–3.56, 3.62–3.70, 3.85–3.92, 3.96–4.07 (4m, 5 H, H-3,4,5,6,7), 4.40–4.83 (4 AB, 8 H, 4 Ph-CH_2), and 7.11–7.36 (m, 20 H, 4 C_6H_5); ^{13}C-n.m.r ($CDCl_3$): δ 38.28 (C-2), 51.53 (OCH_3), 67.54, 70.47 (C-3,7), 71.10 (C-8) 72.86, 73.38, 74.78 (4 Ph-*C*H_2), 76.95, 78.72, 79.98 (C-4,5,6), 127.72–128.33 (*C*H(Ph)), 137.83 (C-*ipso*), and 172.38 (C = O).

Anal. Calc. for $C_{37}H_{42}O_8$: C, 72.29; H, 6.88. Found: C, 71.90; H, 6.99.

*(2*E*,4*E*)-Methyl* (**5**) *and benzyl 4,6,8-tri-*O*-benzyl-2,3,5-trideoxy-*D*-erythro-oct-2,4-dienonate* (**6**). — Tributylphosphine (2.6 mL, 10.5 mmol) and methyl bromoacetate (1.0 mL, 10.5 mmol) were stirred in benzene for 2 h at reflux. Evaporation of the benzene afforded pure tributyl(carbomethoxymethyl)phosphonium bromide (m.p. 59–62°). This salt (1.2 g, 3.4 mmol) was dissolved in toluene (8 mL), butyllithium in hexane (3.4 mmol) was slowly added, and the solution was stirred for 10 min at room temper-

ature. 2,3,4,6-Tetra-*O*-benzyl-α,β-D-glucopyranose (1; 1 g, 1.85 mmol) was added and the mixture was heated at reflux for 20 h. Chromatographic purification on silica gel in 17:3 hexane–ethyl acetate afforded products **5** and **6**.

Compound **5**. Syrup, R_F 0.13 (4:1 hexane–EtOAc); ^{1}H-n-m-r ($CDCl_3$): δ 3.60–3.67 (m, 2 H, H-8a,8b), 3.76 (s, 3 H, OCH_3) 3.8–3.9 (m, 1 H, H-7) 4.11, 4.42 (AB, 2 H, Ph-CH_2), 4.42 (dd, 1 H, $J_{5,6}$ 9.5, $J_{6,7}$ 5.6 Hz, H-6), 4.50, 4.71 (2 s, 4 H, 2 Ph-CH_2), 4.50 (d, 1 H, $J_{5,6}$ 9.5 Hz, H-5), 6.15 (d, 1 H, $J_{2,3}$ 15.7 Hz, H-3), and 6.90–7.46 (m, 21 H, 4 C_6H_5 and H-2); ^{13}C-n.m.r ($CDCl_3$): δ 51.68 (OCH_3), 70.57, 70.74, 73.35, 74.27 (C-8, 3 Ph-CH_2), 72.16, 73.60 (C-6,7), 119.36, 123.75 (C-3,5), 127.67–128.90 (*C*H(Ph)), 137.89–138.04 (*C-ipso*), 139.91 (C-2), 155.16 (C-4), and 167.17 (C = O).

Compound **6**. Syrup, R_F 0.17 (4:1 hexane–ethyl acetate); ^{1}H-n.m.r. ($CDCl_3$): δ 3.46–3.58 (m, 2 H, H-8a,8b), 3.88 (m, 1 H, H-7), 4.24, 4.47 (AB, 2 H, Ph-CH_2), 4.45 (dd, 1 H, $J_{5,6}$ 9.6, $J_{6,7}$ 5,6 Hz, H-6), 4.49, 4.74, 5.23 (3 s, 6 H, Ph-CH_2), 5.53 (d, 1 H, $J_{5,6}$ 9.6 Hz, H-5), 6.23 (d, 1 H, $J_{2,3}$ 15.6 Hz, H-3), and 7.16–7.44 (m, 21 H, 4 C_6H_5 and H-2); ^{13}C-n.m.r ($CDCl_3$): δ 66.42, 70.59, 70.79, 73.37, 74.34, (C-8, 4 Ph-CH_2), 72.20, 73.64 (C-6,7), 119.47, 123.98 (C-3,5), 127.69–128.52 (*C*H(Ph)), 137.95–139.09 (C-*ipso*), 140.22 (C-2), 155.20 (C-4), and 166.31 (C = O).

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