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Note

Synthesis of *C*-glycosyl compounds: the reaction of acetylated glycals with *tert*-butoxycarbonylmethylzinc bromide

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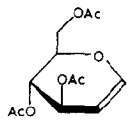
There is increasing interest in *C*-glycosyl compounds because of their potential as enzyme inhibitors[1] and chirons for the synthesis of complex natural products[2]. *C*-Glycosylation procedures variously involve sigmatropic rearrangements[3], addition of a carbon nucleophile at an anomeric centre[4], reactions of glycosyl radicals[5] or carbanions[6], and nucleophilic addition to glycals[7].

We now report on the reactions of the Reformatsky reagent *tert*-butoxycarbonylmethylzinc bromide with the acetylated glycals **1–4**. This reagent was chosen as a model since it is a stable, easily accessible, crystalline compound[8], the CH_2COO^tBu residue can be easily transformed, and a CH_2COOH substituent is "bioisosteric" with a phosphate group[9].



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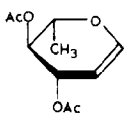

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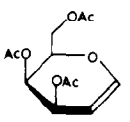

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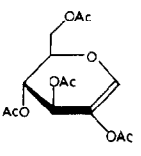

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The reactions were performed by adding the Reformatsky reagent to a solution of each of the glycals **1–4** in the presence of an appropriate catalyst and the results are reported in Table I. Whereas **1–3** reacted to give α,β-mixtures of 2-*C*-glycosylacetic acid derivatives, **4** did not react. The conditions of choice are dichloromethane and trimethylsilyl triflate at 0°C. No reaction occurred in ethereal solvents and no improvement was observed on using titanium tetrachloride at −70°C which also afforded di-*tert*-butyl succinate (~ 15%).

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TABLE I

Reaction of the glycals **1–4** with $BrZnCH_2COO^tBu$

Glycal	Solvent	Catalyst [a]	Time (h)	Temp. (°C)	Yield (%)	Products	α,β-Ratio
1	CH_2Cl_2	a	1	0	48.6	**5**(β) and **6**(α)	2:1
1	$MeOCH_2CH_2OMe$	a	2.4	25	0		
1	CH_2Cl_2	b		−70	0		
2	CH_2Cl_2	a	1	0	48.4	**7**(β) and **8**(α)	1:2
2	CH_2Cl_2	b		−70	42.0	**7**(β) and **8**(α)	1:2
3	CH_2Cl_2	a	1	0	16.1	**9**(β) and **10**(α)	1:2
3	$MeOCH_2CH_2OMe$	a	18	0	0		
4	CH_2Cl_2	a	5	0	0		

[a] a, Trimethylsilyl triflate; b, titanium tetrachloride.

Reaction occurred exclusively at C-1 of each glycal but was not stereospecific, in agreement with the formation of a cationic intermediate, since an α,β-mixture was obtained that could be resolved by chromatography. The α,β-ratios and the yields are controlled by the stereochemistry of the glycal. Thus, 3,4,6-tri-*O*-acetyl-D-glucal (**1**) afforded **5** and **6** (combined yield, 48.6%) in the ratio 1:2, whereas 3,4-di-*O*-acetyl-L-rhamnal (**2**) afforded **7** and **8** (48.4%), and 3,4,6-tri-*O*-acetyl-D-galactal (**3**) afforded **9** and **10** (16.10%), each in the ratio 2:1. The combined yields could be related to the configuration at C-4.

The structures of the *C*-glycosyl compounds **5–10** were assigned on the basis of ^1H and ^{13}C NMR data and molecular modeling techniques, including semiempirical[10] (AM1) and molecular mechanics (MM2, Monte-Carlo[11]) methods.

Compounds **5** and **7**, as expected, each adopted the conformation with all the substituents equatorial and therefore had a high $J_{4,5}$ value (~ 8 Hz). Conformational analysis indicated **6** to be a mixture of the conformers **6a** (78.01%) and **6b** (21.99%), and **8** to be a mixture of the conformers **8a** (83.49%) and **8b** (16.51%) (Table II). The $J_{4,5}$ values for each conformer were calculated using a suitable Karplus-equation[12], and the average $J_{4,5}$ values, calculated on the basis of the conformer populations, were 6.83 Hz for **6** and 6.81 Hz for **8**, which account for the observed values (Table II).

The assignments of the configurations of **5** and **7** were verified by NOE experiments and by ^{13}C NMR data. Irradiation of H-1 (δ 4.55) in **5** caused a 7% enhancement of the H-5 resonance (δ 3.85), and irradiation of H-5 caused an 8% enhancement of the H-1 resonance. Likewise, irradiation of H-1 (δ 4.48) in **7** caused a 7% enhancement in the H-5 resonance (δ 3.8) and irradiation of H-5 caused a 7% enhancement of the H-1 resonance. No NOE was observed between H-1 and H-5 for **6** and **8**. Furthermore, both H-1 and the CH_2COO^tBu resonated at higher field in **5** and **7** which have the CH_2COO^tBu group equatorial, as observed by others[3a],

The $J_{4,5}$ values do not discriminate between **9** and **10**. The β and α configurations were assigned on the basis of the chemical shifts of the H-1 and CH_2COO^tBu

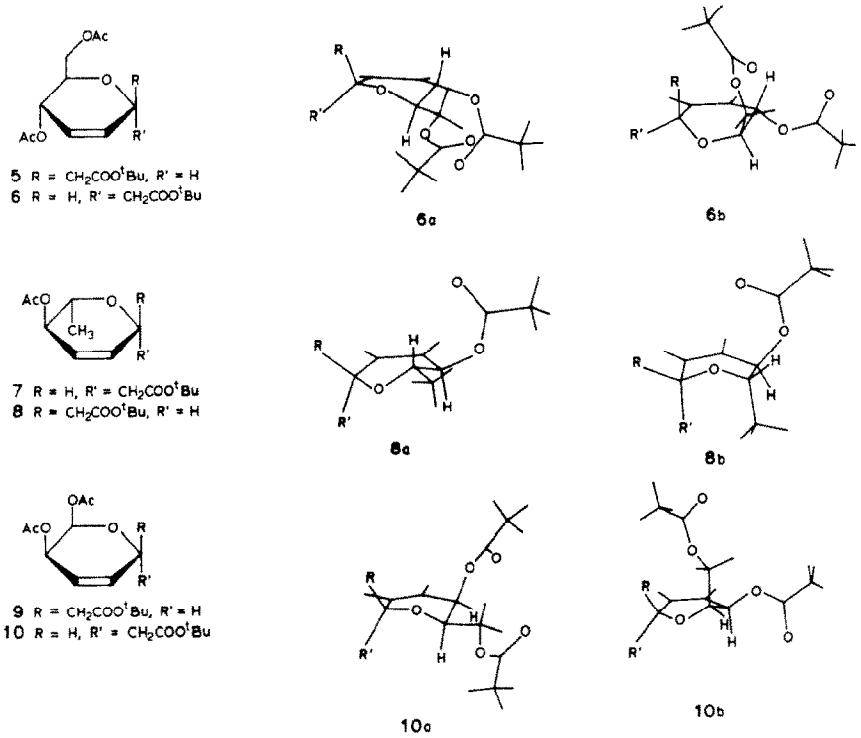

TABLE II

Conformer populations and theoretical $J_{4,5}$ values for **6**, **8**, and **10**

Conformer	E(rel) (kcal/mol)	Population (%)	Φ (°) [a]	$J_{4,5}$ (Hz) [b]
6a	0.00	78.01	171.5	8.54
6b	0.75	21.99	89.2	0.73
			W.A. [c]	6.83
			E. [d]	6.8
8a	0.00	83.49	−177.7	7.73
8b	0.96	16.51	110.1	2.16
			W.A.	6.81
			E.	6.20
10a	0.00	57.54	−53.7	0.49
10b	0.18	42.46	49.1	5.58
			W.A.	2.65
			E.	2.30

[a] Dihedral angle H-4–C-4–C-5–H-5. [b] Calculated for each conformer according to the Haasnoot equation [9]. [c] Weighted average value calculated on the basis of the conformer populations using the 3JHH program [17]. [d] Experimental value.

resonances (both were at higher field in the β anomer **9** as observed for the pairs **5**/**6** and **7**/**8**) and on NOE data. Irradiation of H-1 (δ 4.48) in **9** caused a 7% enhancement in the H-5 resonance (δ 3.88) and irradiation of H-5 caused a similar enhancement of the H-1 resonance. No NOE was observed for **10**. Conformational analysis of the α anomer indicated the presence of the conformations **10a** (57.54%) and **10b** (42.46%), which correspond to an average $J_{4,5}$ value of 2.65 Hz (Table II).

The assignment of the α and β configurations was confirmed by the ^{13}C NMR data. As expected from the γ-gauche effect observed by Stothers[13] in cyclohexane, the α anomers **6** and **10** formed from the D-glucal and D-galactal derivatives (**1** and **3**, respectively) each have the C-5 signal at higher field with respect to the corresponding β anomers **5** and **9**. The same considerations apply to the β anomer from the L-rhamnal derivative **2**.

The above reactions, conducted under mild conditions, allow one-step regioselective introduction of a functionalised C_2 unit at C-1 of acetylated glycals, to give potentially useful synthons.

EXPERIMENTAL

General.—Trimethylsilyl trifluoromethanesulfonate (triflate) and titanium(IV) chloride (M solution in CH_2Cl_2) were purchased from Aldrich, and the glycal derivatives **1**–**4** and $BrZnCH_2COO^tBu$ from Fluka. The Reformatsky reagent was prepared as described[8]. Tetrahydrofuran and 1,2-dimethoxyethane were distilled from $LiAlH_4$. Dichloromethane was distilled from $CaCl_2$. Pyridine was boiled under reflux over KOH (pellets) and then distilled from CaH_2.

IR spectra were recorded with a Perkin–Elmer 681 spectrometer and mass spectra with a VG 7070 EQ spectrometer. 300-MHz ^1H NMR spectra (internal Me_4Si) were obtained with a Bruker AC 300 spectrometer and ^{13}C NMR spectra (200 and 300 MHz) with Varian FT 200 and Bruker AC 300 spectrometers. Column chromatography was performed on silica gel (40–63 μm).

Reactions of acetylated glycals with $BrZnCH_2COO^tBu$.—*(a) 3,4,6-Tri-O-acetyl-D-glucal* (**1**). Trimethylsilyl triflate (0.45 mL, 2.49 mmol) and $BrZnCH_2COO^tBu$ (1.26 M in CH_2Cl_2, 4 mL) were added to a solution of **1** (0.68 g, 2.49 mmol) in CH_2Cl_2 (2.5 mL) at 0°C. The mixture was stirred at 0°C for 30 min, then at room temperature for 30 min, diluted with CH_2Cl_2, washed with water, dried (Na_2SO_4), and concentrated under reduced pressure. Flash-column chromatography[14] (5 : 1 hexane–EtOAc) of the residue gave **5** (16.2%), **6** (32.4%), **1** (40%), and small amounts of unidentified products.

tert-Butyl 2-(4,6-di-*O*-acetyl-2,3-dideoxy-β-D-*erythro*-hex-2-enopyranosyl)acetate (**5**) was isolated as a colorless syrup; $[\alpha]_D$ +53° (*c* 0.3, $CHCl_3$); $\nu_{max}^{CHCl_3}$ 1725, 1720 cm^{-1}. NMR data ($CDCl_3$): ^1H, δ 5.99 (ddd, 1 H, *J* 10.5, 3.0, and 1.3 Hz, H-2), 5.77 (dd, 1 H, *J* 10.5 and 3.1 Hz, H-3), 5.23 (ddd, 1 H, *J* 8.6, 3.1, and 1.3 Hz, H-4), 4.55 (ddd, 1 H, *J* 7.8, 6.5, and 3.0 Hz, H-1), 4.0 and 3.8 (AB part of an ABX system, 2 H, $J_{A,B}$ 10, $J_{A,X}$ 5.6, and $J_{B,X}$ 3.1 Hz, CH_2OAc), 3.72 (ddd, 1 H, *J* 8.6, 5.6, and 3.1

Hz, H-5), 2.50 and 2.36 (AB part of an ABX system, 2 H, $J_{A,B}$ 14.8, $J_{A,X}$ 7.8, and $J_{B,X}$ 6.5 Hz, CH_2COO^tBu), 2.05 (s, 6 H, 2 Ac), and 1.45 (s, 9 H, ^{t}Bu); ^{13}C, δ 170.9 (s), 170.7 (s), 169.9 (s), 132.3 (d), 126.0 (d), 81.3 (s), 74.4 (d), 70.2 (d), 65.2 (d), 62.9 (t), 41.7 (t), 28.5 (q), 21.4 (q), and 21.2 (q). Mass spectrum: *m/z* 255 [$M^+ - {}^t$BuO], 213 [$M^+ - CH_2COO^tBu$], 195 [255 – AcOH], 153 [213 – AcOH], 152 [$M^+ - CH_2{=}CMe_2$ – 2 AcOH]. Anal. Calcd for $C_{16}H_{24}O_7$: C, 58.54; H, 7.3. Found: C, 58.32; H, 7.1.

tert-Butyl 2-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosyl)acetate (**6**) was isolated as a colorless syrup; $[\alpha]_D$ +45° (*c* 0.4, $CHCl_3$); $\nu_{max}^{CHCl_3}$ 1725, 1720 cm^{-1}. NMR data ($CDCl_3$): ^{1}H, δ 6.08 (ddd, 1 H, *J* 10.0, 2.0, and 1.5 Hz, H-2), 5.86 (ddd, 1 H, *J* 10.0, 3.0, and 2.0 Hz, H-3), 5.14 (ddd, 1 H, *J* 6.8, 3.0, and 2.0 Hz, H-4), 4.65 (dddd, 1 H, *J* 8.0, 6.5, 2.0, and 1.5 Hz, H-1), 4.22 and 4.10 (AB part of an ABX system, 2 H, $J_{A,B}$ 11, $J_{A,X}$ 6.2, $J_{B,X}$ 3.1 Hz, CH_2OAc), 3.9 (ddd, 1 H, *J* 6.8, 6.2, and 3.1 Hz, H-5), 2.60 and 2.44 (AB part of an ABX system, 2 H, $J_{A,B}$ 14.8, $J_{A,X}$ 8.0, and $J_{B,X}$ 6.5 Hz, CH_2–COO^tBu), 2.05 (s, 6 H, 2 Ac), and 1.45 (s, 9 H, ^{t}Bu); ^{13}C, δ 171.1 (s), 170.7 (s), 169.9 (s), 132.4 (d), 125. 0 (d), 81.3 (s), 69.5 (d), 67.9 (d), 67.6 (d), 61.8 (t), 40.1 (t), 28.5 (q), 21.4 (q), and 21.2 (q). Mass spectrum: *m/z* 255, 213, 195, 153, and 152. Anal. Found: C, 58.28; H, 7.1.

(*b*) *3,4-Di-*O*-acetyl-*L*-rhamnal* (**2**). The reaction was carried out as described in (*a*). Flash-column chromatography (5:1 hexane–EtOAc) of the products afforded **7** (16.2%), **8** (32.2%), **2** (40%), and small amounts of unidentified products.

tert-Butyl 2-(4-*O*-acetyl-2,3,6-trideoxy-β-L-*erythro*-hex-2-enopyranosyl)acetate (**7**) was isolated as a colorless syrup; $[\alpha]_D$ −83° (*c* 2.1, $CHCl_3$) ; $\nu_{max}^{CHCl_3}$ 1730, 1725 cm^{-1}. NMR data ($CDCl_3$): ^{1}H δ 5.83 (ddd, 1 H, *J* 10.4, 1.5, and 1.0 Hz, H-3), 5.70 (ddd, 1 H, *J* 10.4, 2.2, and 2.2 Hz, H-2), 5.2 (ddd, 1 H, *J* 8.9, 2.2, and 1.5 Hz, H-4), 4.50 (dddd, 1 H, *J* 7.5, 6.5, 2.2, and 1.0 Hz, H-1), 3.8 (dq, 1 H, *J* 8.9 and 7.2 Hz, H-5), 2.54 and 2.28 (AB part of an ABX system, 2 H, $J_{A,B}$ 15.5, $J_{A,X}$ 7.5, and $J_{B,X}$ 6.5 Hz, CH_2COO^tBu), 2.08 (s, 3 H, Ac), 1.45 (s, 9 H, ^{t}Bu), and 1.22 (d, 3 H, *J* 7.2 Hz, H-6,6,6); ^{13}C, δ 170.6 (s), 170.0 (s), 131.86 (d), 126.03 (d), 80.9 (s), 72.50 (d), 71.6 (d), 70.90 (d), 41.60 (t), 28.10 (q), 21.1 (q), and 18.4 (q). Mass spectrum: *m/z* 210 [M^+ – AcOH], 197 [$M^+ - {}^t$BuO), 170 [$M^+ - CH_2{=}CMe_2 - CO_2$], 155 [$M^+ - CH_2{=}CMe_2$ – AcOH], 153 [210 – ^{t}Bu], 110 [$M^+ - CH_2{=}CMe_2$ – AcOH]. Anal. Calcd for $C_{14}H_{22}O_5$: C, 62.22; H, 8.15. Found: C, 61.98; H, 7.95.

tert-Butyl 2-(4-*O*-acetyl-2,3,6-trideoxy-α-L-*erythro*-hex-2-enopyranosyl)acetate (**8**) was isolated as a colorless syrup; $[\alpha]_D$ −68° (*c* 2.0, $CHCl_3$); $\nu_{max}^{CHCl_3}$ 1725, 1720 cm^{-1}. NMR data ($CDCl_3$); ^{1}H, δ 5.92 (ddd, 1 H, *J* 10.4, 1.8, and 1.8 Hz, H-2), 5.78 (ddd, 1 H, *J* 10.4, 2.2, and 2.0 Hz, H-3), 4.89 (ddd, *J* 6.1, 2.0, 1.8 Hz, H-4), 4.57 (dddd, 1 H, *J* 8.2, 5.1, 2.2, and 1.8 Hz, H-1), 3.85 (dq, 1 H, *J* 6.1 and 7.2 Hz, H-5), 2.58 and 2.42 (AB part of a ABX system, 2 H, $J_{A,B}$ 15.4, $J_{A,X}$ 8.5, and $J_{B,X}$ 6.5 Hz, CH_2COO^tBu), 2.08 (s, 3 H, Ac), 1.45 (s, 3 H, ^{t}Bu), and 1.22 (d, 3 H, *J* 7.2 Hz, H-6,6,6); ^{13}C, δ 171.3 (s), 170.6 (s), 133.1 (d), 126.6 (d), 81.5 (s), 70.1 (d), 69.0 (d), 68.4 (d), 40.7 (t), 28.7 (q), 21.8 (q), and 17.7 (q). Mass spectrum: *m/z* 210, 197, 170, 155, 153, and 110. Anal. Found: C, 61.94; H, 7.95.

(*c*) *3,4,6-Tri-O-acetyl-D-galactal* (**3**). The reaction was performed as described in (*a*). Flash-column chromatography (5:2 hexane–EtOAc) of the products gave **9** (10.4%), **10** (5.7%), and **3** (58.9%).

tert-Butyl 2-(4,6-di-*O*-acetyl-2,3-dideoxy-β-D-*threo*-hex-2-enopyranosyl)acetate (**9**) was isolated as a colorless syrup; $\nu_{max}^{CHCl_3}$ 1725, 1720 cm^{-1}. NMR data ($CDCl_3$): ^1H, δ 6.2–5.8 (m, 2 H), 4.48 (dddd, 1 H, *J* 7.2, 6.5, 1.0, and 1.0 Hz, H-1), 5.08 (ddd, 1 H, *J* 3.0, 2.3, and 1.8 Hz H-4), 3.88 (ddd, 1 H, *J* 6.5, 6.5, and 2.3 Hz, H-5), 4.18 (d, 2 H, *J* 6.5 Hz, CH_2OAc), 2.50 and 2.40 (AB part of an ABX system, 2 H, $J_{A,B}$ 14.4, $J_{A,X}$ 7.2, and $J_{B,X}$ 6.5 Hz, CH_2COO^tBu), 2.05 (s, 3 H, Ac), 2.01 (s, 3 H, Ac), and 1.45 (s, 9 H, ^{t}Bu); ^{13}C, δ 171.4 (s), 171.2 (s), 170.3 (s), 134.6 (d), 123.1 (d), 81.7 (s), 74.43 (d), 72.59 (d), 64.09 (d), 63.7 (t), 41.5 (t), 28.7 (q), 21.6 (q), and 21.5 (q). Mass spectrum: *m/z* 255 [$M^+ - {}^t$BuO], 213 [$M^+ - CH_2COO^tBu$], 195 [255 – AcOH], 151 [213 – AcOH], 152 [$M^+ - CH_2{=}CMe_2$ – AcOH]. Anal. Calcd for $C_{16}H_{24}O_7$: C, 58.54; H, 7.3. Found: C, 58.20; H, 6.89.

tert-Butyl 2-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*threo*-hex-2-enopyranosyl)acetate (**10**) was isolated as a colorless syrup; $\nu_{max}^{CHCl_3}$ 1725, 1720 cm^{-1}. NMR data ($CDCl_3$): ^1H, δ 6.1–5.8 (m, 2 H), 5.08 (ddd, 1 H, *J* 3.0, 2.3, and 1.8 Hz, H-4), 4.75 (dddd, 1 H, *J* 8.8, 6.3, 1.5, and 1.0, H-1), 4.08 (ddd, 1 H, *J* 14.0, 6.3, and 2.3 Hz, H-5), 4.2 and 4.0 (AB part of an ABX system, 2 H, $J_{A,B}$ 14.0, $J_{A,X}$ 12.0, and $J_{B,X}$ 6.25 Hz, CH_2OAc), 2.56 and 2.43 (AB part of an ABX system, $J_{A,B}$ 14.0, $J_{A,X}$ 8.8, and $J_{B,X}$ 6.3 Hz, CH_2COO^tBu), 2.05 (s, 3 H, Ac), 2.01 (s, 3 H, Ac), and 1.45 (s, 9 H, ^{t}Bu); ^{13}C, δ 171.4 (s), 171.2 (s), 169.9 (s), 135.5 (d), 123.5 (d), 70.50 (d), 68.77 (d), 64.67 (d), 63.4 (t), 39.4 (t), 28.7 (q) 21.6 (q), and 21.5 (q). Mass spectrum: *m/z* 255, 213, 195, 152 and 151. Anal. Found: C, 58.25; H, 7.0.

Molecular modeling.—Conformational analysis was performed using the AM1 algorithm[10] as implemented in the AMPAC package[15] (to optimise the cyclohexene ring) and a Monte-Carlo algorithm[11] implemented in MAD[16] (to optimise the side chains). Both AM1 and Monte Carlo calculations were performed on an IBM Risc System/6000 (Model 520).

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