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Note

Synthesis of alkyl and aryl *C*-pyranosides using organozinc reagents via a Ferrier-type rearrangement

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Abstract—The reaction of 1,2-dihydropyranyl acetates with dimethylzinc, diethylzinc and diphenylzinc in the presence of CF_3COOH gave the corresponding alky and aryl *C*-pyranosides via a Ferrier rearrangement in excellent yields. Use of the organozinc species, CF_3CO_2ZnPh, reacted with high stereoselectivity to give the phenyl *C*-glycosides. Arylzinc chlorides could also be successfully applied to this reaction in the presence of $BF_3{\cdot}OEt_2$.

Keywords: Organozinc reagents; Alkyl and aryl *C*-pyranosides; Ferrier rearrangement

Alkyl and aryl *C*-pyranosides are valuable synthetic intermediates that can be further functionalized for the preparation of structural units present in many natural biologically active products.[1] Lewis acid-mediated Ferrier rearrangement of glycals with carbon nucleophiles, such as allyltrimethylsilane,[2] olefins,[3] or silyl enol ethers,[4] is widely employed to obtain 2,3-unsaturated *C*-glycosides in good to excellent yields. Organozinc reagents, which can tolerate a broad range of functionalities,[5] can be made to react with per-*O*-acetyl-D-glucal in the presence of $BF_3{\cdot}OEt_2$,[6] TMSOTf[7] and $ZnCl_2$.[8] These reactions afford moderate to good yields of *C*-glycosides preferring α-anomeric selectivity (2–10:1). Herein, we wish to report our preliminary results regarding the addition of organozinc reagents to 1,2-dihydropyranyl acetates for the synthesis of alkyl and aryl *C*-pyranosides.

More recently, the organozinc reagent, CF_3CO_2ZnEt, has been exploited in the nucleophilic ring-opening reaction of epoxides with stereoselectivity.[9] Our continued interest in developing the organozinc reagent, CF_3CO_2ZnR, has prompted us to verify their possibility in the Ferrier rearrangement reaction.

The organozinc reagent, CF_3CO_2ZnEt, can be readily prepared by stirring $ZnEt_2$ with CF_3COOH in CH_2Cl_2 at 0 °C for 30 min. Treatment of 3,4,6-tri-*O*-acetyl-D-glucal (**1**) with the in situ generated CF_3CO_2ZnEt in CH_2Cl_2 at room temperature for 5 h afforded the desired product with a 2.5:1 ratio of α and β anomers in combined 90% yield (entry 1 in Table 1). The ratio of α and β isomers was established by the ^1H NMR spectra of the crude products. In the presence of Lewis acids such as $ZnCl_2$, $ZnBr_2$, or $BF_3{\cdot}OEt_2$ as activators the reaction of (**1**) with CF_3CO_2ZnEt gave the product **2a** with high yield in shorter reaction times. But these Lewis acids showed little effect on the ratio of α and β anomers. The choice of Et_2O as solvent afforded a 34% yield of **2a** after stirring 10 h (entry 6 in Table 1). Reactions performed in THF gave only small amounts of the corresponding product after lengthy reaction times (21 h). The organozinc species, $CF_3CF_2CF_2CO_2ZnEt$, afforded a slightly lower 82% yield under similar reaction conditions. However, CF_3SO_3ZnEt gave only a 61% yield of the desired product after stirring for 7 h at room temperature.

Glycosidation of **1** with dimethylzinc in the presence of CF_3COOH proceeded smoothly to give the corresponding glycoside **2b** in 97% yield (entry 1 in Table 2). Interestingly, the reaction of **1** with diphenylzinc in the presence of CF_3COOH afforded the phenyl glycoside

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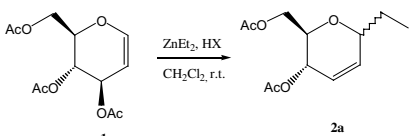
Table 1. Addition of $ZnEt_2$ to 3,4,6-tri-*O*-acetyl-D-glucal (**1**)

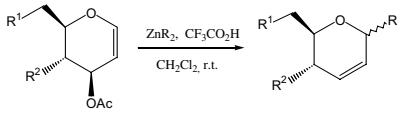


1 **2a**

Entry	Solvent	HX	Activator (1.0 equiv)	Time, h	Yield[a], %	α:β[b] %
1	CH_2Cl_2	CF_3CO_2H	None	4	90	2.5:1
2[c]	CH_2Cl_2	CF_3CO_2H	$ZnCl_2$	10	70	3.0:1
3	CH_2Cl_2	CF_3CO_2H	$ZnCl_2$	2	87	2.5:1
4	CH_2Cl_2	CF_3CO_2H	$ZnBr_2$	3	95	2.1:1
5	CH_2Cl_2	CF_3CO_2H	$BF_3{\cdot}OEt_2$	2	96	2.5:1
6	Et_2O	CF_3CO_2H	None	10	34	2.7:1
7	Et_2O	CF_3CO_2H	$BF_3{\cdot}OEt_2$	10	91	2.8:1
8	CH_2Cl_2	$C_4F_9CO_2H$	None	5	82	2.0:1
9	CH_2Cl_2	CF_3SO_3H	None	7	61	2.4:1

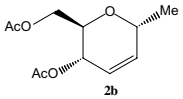
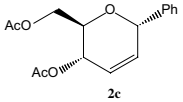
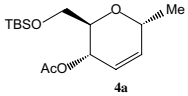
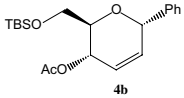
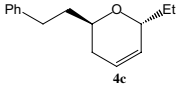
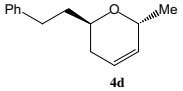
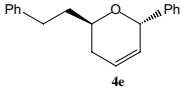
[a] Isolated yields.
[b] The α:β ratios were determined by ^1H NMR spectroscopy of the crude products.
[c] The reaction was carried out at 0 °C.

Table 2. Addition of ZnR_2 to **1** and **3a, b** in the presence of CF_3COOH



3a: R^1 = TBSO; R^2 = AcO
3b: R^1 = $PhCH_2$; R^2 = H

4

Entry	ZnR_2	Product	Time, h	Yield[a], %	α:β[b]
1	$ZnMe_2$	 **2b**	3	97	2.3:1
2	$ZnPh_2$	 **2c**	2	90	10:1
3	$ZnMe_2$	 **4a**	3	89	5:1
4	$ZnPh_2$	 **4b**	3	88	19:1
5	$ZnEt_2$	 **4c**	1.5	89	10:1
6	$ZnMe_2$	 **4d**	1.5	98	10:1
7	$ZnPh_2$	 **4e**	1.5	87	20:1

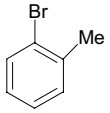
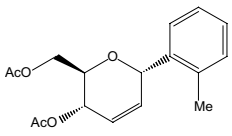
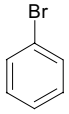
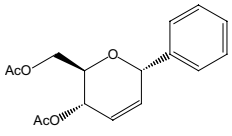
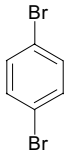
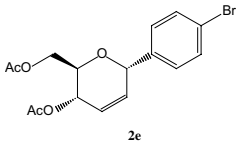
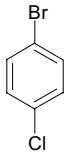
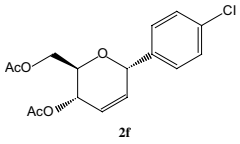
[a] Isolated yields after purification by column chromatography.
[b] The α:β ratios were determined by ^1H NMR spectroscopy of the crude products.

with 10:1 α:β selectivity in 90% yield (entry 2 in Table 2). Extension of the organozinc species CF_3CO_2ZnR to other substrates furnished the corresponding products in excellent yields. Treatment of compound **3a** with the organozinc reagent, CF_3CO_2ZnMe, gave the desired product **4a** with a 5:1 ratio of α and β anomers in combined 89% yield (entry 3 in Table 2). The addition of CF_3CO_2ZnPh to **3a** provided in **4b** 88% yield with high selectivity (α:β = 19:1). The stereoselectivity difference between the reaction of glycals and with the organozinc species, CF_3CO_2ZnR, seems to indicate that substituents at C-6 and nucleophiles exert a significant influence on the ratio of α and β anomers. Substituent factors contributing to the stereoselectivity in the reaction of tetrahydropyran acetals with allyltrimethylsilane have been explored by Woerpel and co-workers.[10] Furthermore, 1,2-dihydropyranyl acetate **3b** when submitted to this reaction gave the corresponding products in excellent yields and high α selectivity (α:β ⩾ 10:1) (entries 5–7 in Table 2). These results suggest that organozinc species, CF_3CO_2ZnR, which can be easily formed, provide a simple and practical method for the synthesis of alkyl and aryl *C*-pyranosides.

Encouraged by the initial results using $ZnPh_2$ in the presence of CF_3CO_2H with good stereocontrol, we wish to extend further the organozinc species ArZnX, which can be easily prepared from ArLi and $ZnCl_2$, as nucleophiles to this reaction. Although per-*O*-acetyl-D-glucals have been frequently used as suitable donors in the carbon–Ferrier rearrangement, to our knowledge, few examples of the aryl glycosidations of 3,4,6-tri-*O*-acetyl-D-glucal **1** with arylzinc reagents have been described.[11–13] The results of glycosidation of **1** with ArZnCl are summarized in Table 3. The reaction of glycal with *o*-$CH_3C_6H_4ZnCl$ in CH_2Cl_2 at room temperature for 12 h gave only a small amount of **2d**. Interestingly, moderate yields were obtained in the presence of $BF_3{\cdot}OEt_2$ as activator (entries 1–2 in Table 3). Notably, the solvents have an important influence on the reaction efficiencies. The reaction mixture stirring in Et_2O solvent led to rapid consumption (1 h, rt) of starting materials afforded the corresponding product **2d** with 7:1 α:β selectivity in 97% yield (entry 3 in Table 3). However, no desired product was obtained when the reaction was carried out in Et_2O solvent in the absence of $BF_3{\cdot}OEt_2$. Mixing of **1** with an Et_2O solution of PhZnCl in the presence of $BF_3{\cdot}OEt_2$ gave **2c** in 98% yield with a slightly lower α:β selectivity (6:1) in comparison with the CH_2Cl_2 solution of $ZnPh_2$ in the presence of CF_3 CO_2H (entry 4 in Table 3 vs entry 2 in Table 2). Similarly, the reaction of **1** with *p*-BrC_6H_4ZnCl and *p*-ClC_6H_4ZnCl also furnished the corresponding glycosides **2e** and **2f** in 94% (α:β 7:1) and 86% (α:β 8:1) yields, respectively.

In conclusion, we have demonstrated a new and simple method for the synthesis of 2,3-unsaturated alkyl

Table 3. Addition of ArZnCl to **1** in the presence of $BF_3{\cdot}OEt_2$

Entry	ArBr	Product	Time, h	Yield[a], %	α:β[b]
1[c]		 **2d**	8	42	7:1
2[d]			5	56	7:1
3			1	97	7:1
4		 **2c**	2	98	6:1
5		 **2e**	2	94	7:1
6		 **2f**	1	86	8:1

[a] Isolated yields after purification by column chromatography.
[b] The α:β ratios were determined by ^1H NMR spectroscopy of the crude products.
[c] The reaction was performed in CH_2Cl_2 using 1.0 equiv of $BF_3{\cdot}OEt_2$.
[d] Performed in CH_2Cl_2 using 2.0 equiv of $BF_3{\cdot}OEt_2$.

and aryl *C*-pyranosides using organozinc reagents. Dimethylzinc and diethylzinc afforded the corresponding products in high yields with 2–10:1 α:β selectivity in the presence of CF_3CO_2H, whereas diphenylzinc provided an efficient and high stereoselectivity route to the synthesis of phenyl pyranosides. Arylzinc chlorides can also be successfully applied to the synthesis of aryl *C*-glycosides from 3,4,6-tri-*O*-acetyl-D-glucal in the presence of $BF_3{\cdot}OEt_2$.

1. Experimental

1.1. General methods

IR spectra were recorded on a Perkin–Elmer FT210 spectrophotometer. ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were measured with a Bruker AC 300 spectrometer using Me_4S as the internal standard. Column chromatography was performed on silica gel (100–200 mesh), and analytical TLC was carried out on silica gel 60-F_{254} plates (Qindao) with detection by fluorescence and then charring with a 10% ethanolic solution of sulfuric acid. High-resolution mass spectra were obtained with a Micromass GCT TOF mass spectrometer.

The following compounds were prepared essentially as described in the literature:

C-(4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosyl)ethane (**2a**),[6a] *C*-[4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosyl]methane (**2b**),[14] *C*-[4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosyl]benzene (**2c**),[11] 1-*C*-[4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosyl]-2-methylbenzene (**2d**),[11] 1-*C*-[4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosyl]-4-chlorobenzene (**2f**),[11] and *trans*-5,6-Dihydro-6-phenethyl-2-phenyl-2*H*-pyran (**4e**).[8]

1.1.1. Standard procedure for preparation of alkyl and aryl *C*-pyranosides with ZnR_2 in the presence of CF_3COOH. To a solution of ZnR_2 (0.6 mmol, 2.0 equiv) in 1.0 mL of CH_2Cl_2 at 0 °C was added dropwise CF_3COOH (46 μL, 0.6 mmol, 2.0 equiv) slowly via syringe under N_2. After stirring for 30 min at 0 °C, a solution of 1,2-dihydropyranyl acetates (0.3 mmol, 1.0 equiv) in 1.0 mL of CH_2Cl_2 was added. The mixture was stirred at room temperature until TLC indicated complete consumption of the starting glucal. The reaction was quenched by addition of 1.0 mL satd aq NH_4Cl and extracted with Et_2O (3×10 mL). The combined organic extracts was washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure to an oily residue. The desired product was purified by silica gel chromatography using 20:1–15:1 petroleum ether–EtOAc.

1.1.1.1. *C*-4-*O*-Acetyl-[6-*O*-(*tert*-butyldimethylsilyl)-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosyl]methane (4a). IR (neat, cm^{-1}) 2956, 1743, 1466, 1237, 1192, 1049, 970, 839, 779; ^1H NMR ($CDCl_3$, 300 MHz) (α-anomer): δ 5.87 (td, *J* 1.4, 10.1 Hz, 1H), 5.78 (td, *J* 2.2, 10.1 Hz, 1H), 5.11 (m, 1H), 4.38–4.35 (m, 1H), 3.82–3.71 (m, 3H), 2.08 (s, 3H), 1.29 (d, *J* 6.8 Hz, 3H), 0.90 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) (α-anomer): δ 170.7, 135.2, 122.9, 73.2, 67.6, 65.5, 62.9, 29.9, 26.0, 21.4, 19.6, −5.2, −5.3; ^1H NMR ($CDCl_3$, 300 MHz) (β-anomer): δ 5.78 (m, 1 H), 5.71 (m, 1H), 5.21 (m, 1H), 4.23 (m, 1H), 3.82–3.71 (m, 2H), 3.57 (m, 1H), 2.06 (s, 3H), 1.23 (d, *J* 6.7 Hz, 3H), 0.90 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H); HRCIMS: Calcd for $C_{15}H_{29}O_4Si$, *m*/*z* 301.1835 $[MH]^+$. Found: *m*/*z* 301.1840.

1.1.1.2. *C*-4-*O*-Acetyl-[6-*O*-(*tert*-butyldimethylsilyl)-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosyl]benzene (4b). IR (neat, cm^{-1}) 2931, 1740, 1494, 1095, 973, 838, 779, 700; ^1H NMR ($CDCl_3$, 300 MHz) for α-anomer: δ 7.44–7.33 (m, 5H), 6.16 (br d, *J* 10.3 Hz, 1H), 5.99 (br d, *J* 10.3 Hz, 1H), 5.29 (m, 2H), 3.74 (m, 3H), 2.08 (s, 3H), 0.87 (s, 9H), 0.07 (s, 3H), 0.04 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 170.6, 139.5, 131.9, 128.5, 128.0, 127.8, 124.9, 73.5, 72.4, 65.5, 63.1, 25.9, 21.3, 18.4, −5.4, −5.3; HRCIMS: Calcd for $C_{20}H_{31}O_4Si$, *m*/*z* 363.1992 $[MH]^+$. Found: *m*/*z* 363.1986.

1.1.1.3. *trans*-5,6-Dihydro-2-ethyl-6-phenethyl-2-phenyl-*H*-pyran (4c). IR (neat, cm^{-1}) 3030, 2963, 1602, 1454, 1261, 1023, 801, 699; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.27–7.15 (m, 5H), 5.75–5.70 (m, 2H), 4.05 (m, 1H), 3.65 (m, 1H), 2.84 (m, 1H), 2.66 (m, 1H), 1.96–1.87 (m, 3H), 1.73 (m, 1H), 1.58 (m, 1H), 1.48 (m, 1H), 1.00 (t, *J* 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 142.5, 129.9, 128.6, 128.4, 125.8, 123.9, 74.1, 67.1, 37.3, 32.2, 30.1, 27.3, 10.7; HREIMS: Calcd for $C_{15}H_{20}O$, *m*/*z* 216.1514 $[M]^+$. Found: *m*/*z* 216.1518.

1.1.1.4. *trans*-5,6-Dihydro-2-methyl-6-phenethyl-2*H*-pyran (4d). IR (neat, cm^{-1}) 3029, 2926, 1604, 1495, 1454, 1365, 1240, 1051, 952, 750, 700; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.22–7.09 (m, 5H), 5.69–5.66 (m, 2H), 4.30 (m, 1H), 3.60 (m, 1H), 2.72 (m, 1H), 2.61 (m, 1H), 1.90–1.66 (m, 4H), 1.17 (d, *J* 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 142.3, 131.0, 128.6, 128.3, 125.8, 123.5, 68.5, 66.6, 37.0, 31.9, 30.7, 20.1; HREIMS: Calcd for $C_{14}H_{18}O$, *m*/*z* 203.1436 $[M]^+$. Found: *m*/*z* 203.1439.

1.1.2. Standard procedure for preparation of aryl *C*-glycosides with ArZnCl.

To a solution of aryl halide (0.6 mmol, 2.0 equiv) in Et_2O (1.5 mL) at 0 °C was added dropwise a solution of 2.5 M *n*-BuLi (240 μL, 0.6 mmol, 2.0 equiv). The mixture was stirred at room temperature for 30 min, then a solution of $ZnCl_2$ (82 mg, 0.6 mmol, 2.0 equiv) in 1.0 mL of Et_2O was added via syringe at 0 °C. Transfer of the $ZnCl_2$ was made quantitative with an additional 0.5 mL of Et_2O. After the white suspension was stirred at room temperature for 1 h, a solution of 3,4,6-tri-*O*-acetyl-D-glucal (81.6 mg, 0.3 mmol) in 1.5 mL of Et_2O was added at −78 °C, followed by addition of $BF_3{\cdot}Et_2O$ (159 μL, 0.6 mmol, 2.0 equiv). Then the reaction flask was moved from the cold bath and stirred for 1–2 h at room temperature. The reaction was quenched by addition of 2.5 mL of satd aq NH_4Cl and extracted with Et_2O (3 × 10 mL). The combined organic extracts was washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The desired product was isolated by silica gel chromatography with 15:1 petroleum ether–EtOAc.

1.1.2.1. 1-*C*-[4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosyl]-4-bromobenzene (2e). IR (neat, cm^{-1}) 2953, 1740, 1370, 1233, 1047, 801; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.45 (d, *J* 8.1 Hz, 2H), 7.23 (d, *J* 8.1 Hz, 2H), 6.08 (d, *J* 9.8 Hz, 1H), 5.94 (d, *J* 9.8 Hz, 1H), 5.22–5.11 (m, 2H), 4.20 (dd, *J* 6.0, 11.7 Hz, 1H), 4.03 (dd, *J* 2.4, 11.7 Hz, 1H), 3.76–3.75 (m, 1H), 2.05 (s, 3H), 2.03 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 170.7, 170.3, 130.0, 131.7, 130.9, 129.6, 125.4, 122.3, 73.0, 69.5, 64.9, 62.8, 21.0, 20.8. HRCIMS: Calcd for $C_{16}H_{18}BrO_5$, *m*/*z* 369.0337 $[MH]^+$. Found: *m*/*z* 369.0338.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carres.2004.11.012.

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