Anal. Calcd for $C_{26}H_{32}N_2ICl$: C, 58.38; H, 6.03; N, 5.24. Found: C, 58.15; H, 6.15; N, 5.04.

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Palladium-Mediated Coupling of a 3-Deoxy Pyranoid Glycal: Stereochemistry of *C*-Glycosyl Bond Formation

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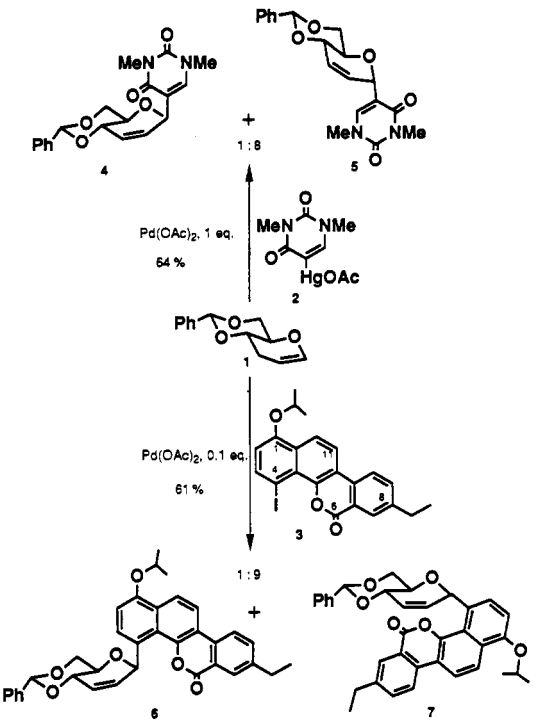
A direct and efficient synthetic route to *C*-glycosides involves palladium-mediated coupling of furanoid or pyranoid glycals (1,2-unsaturated carbohydrates) with appropriate aryl or heterocyclic aglycon derivatives.[1,2] Typical glycals, which bear hydroxy or substituted hydroxy groups (acetoxy, alkoxy, silyloxy) at the allylic (C-3) carbon, undergo palladium-mediated coupling with formation of a *C*-glycosyl bond in a regio-[3] and stereospecific[4] sense. We have now extended this study to include a 3-deoxy pyranoid glycal, 1,5-anhydro-2,3-dideoxy-4,6-*O*-(phenylmethylene)-D-*erythro*-hex-1-enitol[5] (1), in which the allylic (C-3) carbon bears only hydrogen. Pyranoid glycal 1 was subjected to palladium-mediated coupling reactions with (1,3-dimethyl-1,2,3,4-tetrahydro-2,4-dioxopyrimidin-5-yl)mercuric acetate[6] (2) in the presence of stoichiometric palladium(II) acetate and with 8-ethyl-4-iodo-1-[(1-methylethyl)oxy]benzo[*d*]naphtho[1,2-*b*]pyran-6-one (3) in the presence of a catalytic portion of palladium acetate.[7] In each of these coupling reactions, a mixture of anomeric α- and β-*C*-glycosides was produced.

Reaction of 3-deoxy glycal 1[5] with organomercurial 2[6] in the presence of stoichiometric palladium acetate in acetonitrile at room temperature yielded a 1:8 mixture of two stereoisomeric *C*-glycosides (4 and 5), which are β- and α-anomers, respectively. Products 4 and 5 were separated from the reaction mixture by sequential silica gel column and thin layer chromatographic steps in 7% and 57% yields, respectively. The β-anomer (4), produced in this reaction, was indistinguishable from an authentic sample synthesized previously by a different route.[8] In a similar reaction, involving palladium-mediated coupling under catalytic conditions,[9] 3-deoxy glycal 1[5] and iodo aglycon derivative 3 produced an anomeric pair of anthracyclic *C*-glycosides (6 and 7) in a ratio of 1:9 (61% combined yield).

In previous studies involving pyranoid glycals[1,7,10-12] attack of the intermediate organopalladium reagent derived from the aglycon derivative (e.g. 2 or 3) has occurred invariably from the face of the glycal opposite the C-3 oxy substituent.[1] In 3-deoxy glycal 1, the remaining chiral centers at C-4 and C-5 are sufficiently remote that approach of the organopalladium reagent to either face of the glycal double bond for π-complex formation[1] appears unimpeded. Nonetheless, as the present results make clear, the absence of stereodirecting groups at C-3 does not preclude significant stereocontrol of π-complex and *C*-glycosyl bond formation. Asymmetry at the more remote sites of the glycal, C-4 and C-5, effects high (8 or 9 to 1) reaction stereoselectivity. This result indicates that a stereo-directing group at carbon C-3 is not essential for synthetically efficient construction of a stereocontrolled *C*-glycosyl linkage.[1]



It is noteworthy that the present result is important in a second respect. Palladium-mediated coupling of a 3-deoxy glycal with an appropriate aglycon derivative leads to intermediate σ-organopalladium adducts (8 and 9, respectively) which must, invariably, decompose to form products by syn β-hydride elimination.[13] This represents

† Lehigh University.

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(3) Note that similar coupling reactions involving acyclic enol ethers often produce regioisomeric mixtures; see: (a) Daves, G. D., Jr.; Hallberg, A. *Chem. Rev.* **1989**, *89*, 1433-1445. (b) Andersson, C.-M.; Hallberg, A.; Daves, G. D., Jr. *J. Org. Chem.* **1987**, *52*, 3529-3536.
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(6) Arai, I.; Daves, G. D., Jr., *J. Org. Chem.* **1978**, *43*, 4110-4112.
(7) Formation of the reactive organopalladium reagent from organomercurial 2 by transmetalation requires stoichiometric palladium(II). In contrast, formation of the intermediate organopalladium reagent from an idoaglycon (e.g. 3) occurs by oxidative addition of Pd(0), formed by in situ reduction of Pd(II), to the Ar–I bond; see refs 1 and 3a. Daves, G. D., Jr. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press: Greenwich, CT, in press.
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(12) Bellosta, V.; Czernecki, S.; Avenil, D.; El Bahij, S.; Gillier-Pandraud, H. *Can. J. Chem.* **1990**, *68*, 1364-1368.
(13) We have deliniated several different decomposition modes for the intermediate σ-organopalladium adducts formed in these reactions (see 8 and 9). The absence of a leaving group at C-3 other than hydrogen and the lack of reaction mixture acidity[1,8,10] required for palladium elimination with pyran ring opening, leaves β-hydrogen elimination as the only accessible σ-adduct decomposition mode.[1]

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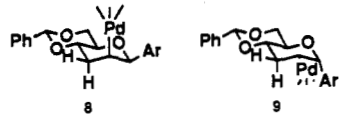
a new example of control of the mode of σ-organopalladium adduct decomposition by selection of an appropriate glycal C-3 substituent.[1,14]



8 9

Experimental Section

General Comments. Thin-layer chromatography (TLC) was carried out on prescored silica gel GF plates (Analtech). Preparative TLC was carried out on 1 mm thick, 20 × 20 cm, silica gel GF plates (Analtech). For flash chromatography, silica gel 60 (230–400 mesh ASTM, E. Merck) was used. Columns were eluted with a positive nitrogen pressure. Nuclear magnetic resonance spectra were obtained on JEOL FX90Q or Bruker AM 500 spectrometers and are referenced to internal tetramethylsilane. Melting points were measured with a Thomas-Hoover capillary apparatus and are uncorrected. Elemental analyses were carried out by Quantitative Technologies, Bound Brook, NJ.

Coupling of 1,5-Anhydro-2,3-dideoxy-4,6-*O*-(phenylmethylene)-D-*erythro*-hex-1-enitol[5] (1) with (1,3-Dimethyl-1,2,3,4-tetrahydro-2,4-dioxopyrimidin-5-yl)mercuric acetate[6] (2). Compound 2[6] (197 mg, 0.494 mmol) and palladium acetate (112 mg, 0.498 mmol) were dissolved in 5 mL of acetonitrile by applying ultrasound for 30 s at room temperature. 3-Deoxy glycal 1[5] (155 mg, 0.74 mmol) was then added. After being stirred for 12 h, the black reaction mixture was filtered through Celite, and solvent was evaporated. The resulting mixture was separated by sequential column and preparative TLC (multidevelopment) using ether/petroleum ether (20:1) as eluent to yield 101 mg (57%) of **5** and 12 mg (7%) of **4** as colorless crystals. The β-anomer, 5-(2′,3′-dideoxy-4′,6′-*O*-(phenylmethylene)-β-D-*erythro*-hex-2-enopyranosyl)-1,3-dimethyl-2,4(1*H*,3*H*)-pyrimidinedione (**4**), mp 190 °C, was indistinguishable from an authentic sample.[8] The α isomer, 5-(2′,3′-dideoxy-4′,6′-*O*-(phenylmethylene)-α-D-*erythro*-hex-2-enopyranosyl)-1,3-dimethyl-2,4(1*H*,3*H*)-pyrimidinedione (**5**), mp 176 °C, exhibited spectra: MS *m/z* 356 ($M^{+\cdot}$); ^{1}H NMR ($CDCl_3$) δ 7.26–7.47 (5 H, phenyl), 7.20 (br, H-6), 6.39 (d, 1 H, $J_{2',3'}$ = 10.3 Hz, H-2′), 5.77 (ddd, 1 H, $J_{3',1'}$ = 2.4 Hz, $J_{3',4'}$ = 2.7 Hz, H-3′), 5.62 (s, 1 H, PhCH), 5.49 (m, 1 H, H-1′), 4.30 (m, 1 H, H4′), 4.19 (m, 1 H, $J_{6'a,6'a}$ = 10 Hz, H-6e′), 3.82 (dd, 1 H, $J_{6'a,5'}$ = 10 Hz, H-6a′), 3.50 (m, 1 H, H-5′), 3.38, 3.42 (6 H, NCH_3); ^{13}C NMR ($CDCl_3$) δ 26.46, 28.00, 31.18, 64.74, 68.35, 69.43, 74.94, 101.73, 110.70, 125.99, 126.95, 127.53, 128.24, 129.02, 129.43, 129.67, 134.71, 137.17, 141.60, 151.41, 162.53.

Anal. Calcd for $C_{19}H_{20}O_5N_2$: C, 64.0; H, 5.66; N, 7.86. Found: C, 63.7; H, 5.33; N, 7.57.

8-Ethyl-1-[(1-methylethyl)oxy]benzo[*d*]naphtho[1,2-*b*]-pyran-6-one. To a mixture of 8-ethyl-1-hydroxybenzo[*d*]-naphtho[1,2-*b*]pyran-6-one[15] **12** (2.0 g, 6.9 mmol), 2-bromopropane (4.2 g, 34.5 mmol), and potassium carbonate (9.5 g, 69 mmol) in 50 mL of dry dimethylformamide was added 18-crown-6 ether (0.5 g, 1.9 mmol). The mixture was then stirred for 10 h at 60 °C at which time TLC indicated that reaction was complete. The volatiles were removed in vacuo; chloroform (100 mL) was then added, and the resulting mixture was filtered through a small amount of silica gel. The filtrate was washed three times with water and dried over sodium sulfate. The volatiles were removed, and the residue was recrystallized from chloroform–ethanol to give 1.95 g (85%) of 8-ethyl-1-[(1-methylethyl)oxy]benzo[*d*]-naphtho[1,2-*b*]pyran-6-one as white crystals: mp 139 °C; ^{1}H NMR ($CDCl_3$) 1.30 (t, 3 H, CH_3), 1.45 (d, 6 H, isopropyl), 2.76 (q, 2 H, benzylic), 4.73 (m, 1 H, isopropyl), 6.91 (d, 1 H, $J_{2,3}$ = 7.8 Hz, H-2), 7.47 (dd, 1 H, $J_{3,4}$ = 8.5 Hz, H-3), 7.62 (dd, 1 H, $J_{7,9}$ = 1.7 Hz, $J_{9,10}$ = 8.1 Hz, H-9), 7.93 (d, 1 H, $J_{11,12}$ = 9.1 Hz), 8.04 (d, 1 H, H–10), 8.08 (d, 1 H, H-4), 8.15 (d, 1 H, $J_{11,12}$ = 9.1 Hz), 8.23 (d, 1 H, H-7); ^{13}C NMR ($CDCl_3$) δ 15.19, 22.04, 28.58, 70.58, 108.16, 113.49, 113.87, 117.94, 118.90, 121.05, 122.12, 125.10, 126.84, 127.18, 129.07, 133.03, 135.01, 145.10, 146.54, 153.45, 161.53.

Anal. Calcd for $C_{22}H_{20}O_3$: C, 79.5; H, 6.07. Found: C, 79.6; H, 5.92.

8-Ethyl-4-iodo-1-[(1-methylethyl)oxy]benzo[*d*]naphtho-[1,2-*b*]pyran-6-one (3). To a mixture of 8-ethyl-1-[(1-methylethyl)oxy]benzo[*d*]naphtho[1,2-*b*]pyran-6-one (150 mg, 0.464 mmol) and *N*-iodosuccinimide (132 mg, 0.586 mmol) in 10 mL of dry dimethylformamide was added 1 drop of concentrated sulfuric acid. The reaction mixture was then stirred at 60 °C for 2 h at which time TLC indicated the reaction was complete. The residue was dissolved in chloroform and washed with a saturated solution of sodium thiosulfate and then with distilled water. The organic layer was dried over sodium sulfate, and the solvent was then removed. The residue was recrystallized from chloroform–ethanol to give 191 mg (92%) of 8-ethyl-4-iodo-1-[(1-methylethyl)oxy]benzo[*d*]naphtho[1,2-*b*]pyran-6-one (**3**) as off-white crystals: mp 215 °C; ^{1}H NMR ($CDCl_3$) δ 1.30 (t, 3 H, CH_3), 1.44 (d, 6 H, isopropyl), 2.76 (q, 2 H, benzylic), 4.69 (m, 1 H, isopropyl), 6.54 (d, 1 H, $J_{2,3}$ = 8.3 Hz, H-2), 7.64 (dd, 1 H, $J_{7,9}$ = 1.8 Hz, $J_{9,10}$ = 8.3 Hz, H-9), 7.99 (d, 1 H, $J_{11,12}$ = 9.0 Hz), 8.05 (d, 1 H, H-10), 8.16 (d, 1 H, H-3), 8.20 (d, 1 H, $J_{11,12}$ = 9.0 Hz), 8.21 (d, 1 H, H-7); ^{13}C NMR ($CDCl_3$) δ 15.21, 21.94, 28.59, 70.90, 73.28, 109.32, 114.67, 118.74, 119.15, 120.94, 122.34, 124.08, 128.60, 128.76, 132.66, 134.98, 142.38, 145.02, 145.50, 153.78, 160.13.

Anal. Calcd for $C_{22}H_{19}IO_3$: C, 57.7; H, 4.18. Found: C, 57.8; H, 4.01.

Coupling of 1,5-Anhydro-2,3-dideoxy-4,6-*O*-(phenylmethylene)-D-*erythro*-hex-1-enitol[5] (1) with 8-Ethyl-4-iodo-1-[(1-methylethyl)oxy]benzo[*d*]naphtho[1,2-*b*]pyran-6-one (3). To a stirred solution of **3** (317 mg, 0.69 mmol), **1** (300 mg, 1.38 mmol), sodium acetate (57 mg, 0.69 mmol), and tri-*n*-butylamine (33 μL, 0.14 mmol) in 25 mL of dry dimethylformamide was added palladium acetate (16 mg, 0.069 mmol). The solution was stirred at room temperature for 6 days, and the volatiles were then removed in vacuo. The resulting residue was dissolved in chloroform and passed through a short column of silica gel. An NMR spectrum of the crude reaction mixture indicated a 1:9 ratio of anomeric *C*-glycosides **6** and **7**, respectively. Purification was accomplished using preparatory TLC (methylene chloride–ether, 50:1) to give 30 mg (8%) of 4-(2′,3′-dideoxy-4′,6′-*O*-(phenylmethylene)-β-*erythro*-hex-2-enopyranosyl)-8-ethyl-1-[(1-methylethyl)oxy]benzo[*d*]naphtho[1,2-*b*]pyran-6-one (**6**), mp 238 °C, and 201 mg (53%) of 4-(2′,3′-dideoxy-4′,6′-*O*-(phenylmethylene)-α-D-*erythro*-hex-2-enopyranosyl)-8-ethyl-1-[(1-methylethyl)oxy]benzo[*d*]naphtho[1,2-*b*]pyran-6-one (**7**), mp 218–220 °C, as white solids which were recrystallized from chloroform–ethanol. For **6**: ^{1}H NMR ($CDCl_3$) δ 1.34 (t, 3 H, *J* = 6.6 Hz, CH_3), 1.47 (dd, 6 H, isopropyl), 2.83 (q, 2 H, benzylic), 3.92 (dd, 1 H, $J_{5',6'}$ = 10.2 Hz, $J_{6',6''}$ = 10.3 Hz, H-6a′), 4.21 (ddd, 1 H, $J_{4',5'}$ = 4.7 Hz, $J_{5',6''}$ = 4.7 Hz, H-5′), 4.47 (m, 2 H, H-4′, H-6e′), 4.79 (m, 1 H, isopropyl), 5.70 (s, 1 H, benzylidene), 6.09 (d, 1 H, $J_{2',3'}$ = 10.3 Hz, H-2′), 6.20 (ddd, 1 H, $J_{1',3'}$ = 2.1 Hz, $J_{3',4'}$ = 4.1 Hz, H-3′), 6.96 (d, 1 H, $J_{2,3}$ = 8.4 Hz, H-2), 7.07 (br, 1 H, H-1′), 7.40, 7.58 (m, 5 H, Ph), 7.72 (dd, 1 H, $J_{7,9}$ = 1.8 Hz, $J_{9,10}$ = 8.2 Hz, H-9), 7.84 (d, 1 H, H-10), 8.07 (d, 1 H, $J_{11,12}$ = 9.1 Hz, H-11), 8.17 (d, 1 H, H-3), 8.28 (d, 1 H, H-7), 8.32 (d, 1 H, H-12); ^{13}C NMR ($CDCl_3$) δ 15.28, 21.96, 22.09, 28.63, 69.73, 70.70, 71.71, 75.54, 76.32, 102.16, 107.72, 115.02, 118.33, 119.60, 120.62, 122.46, 122.76, 125.73, 126.34, 126.38, 127.85, 128.07, 128.32, 128.36, 128.80, 129.04, 129.12, 132.24, 133.08, 135.09, 137.73, 145.41, 147.56, 153.29, 160.56.

Anal. Calcd for $C_{35}H_{32}O_6$: C, 76.6; H, 5.88. Found: C, 76.4; H, 5.67.

For **7**: ^{1}H NMR ($CDCl_3$) δ 1.32 (t, 3 H, *J* = 7.6 Hz, CH_3), 1.48 (d, 6 H, *J* = 6.0 Hz, isopropyl), 2.80 (q, 2 H, benzylic), 3.63 (ddd, 1 H, $J_{4',5'}$ = 8.6 Hz, $J_{5',6'}$ = 4.6 Hz, $J_{5',6''}$ = 10.1 Hz, H-5′), 3.80 (dd, 1 H, $J_{6',6''}$ = 10.3 Hz, H-6a′), 4.02 (dd, 1 H, H-6e′), 4.38 (m, 1 H, H-4′), 4.76 (m, 1 H, isopropyl), 5.62 (s, 1 H, benzylidene), 6.15 (ddd, 1 H, $J_{1',2'}$ = 5.1 Hz, $J_{2',3'}$ = 10.3 Hz, $J_{2',4'}$ = 2.5 Hz, H-2′), 6.24 (d, 1 H, H-3′), 6.86 (d, 1 H, $J_{2,3}$ = 8.3 Hz, H-2), 7.08 (dd, 1 H, H-1′), 7.34, 7.50 (m, 5 H, Ph), 7.66 (d, 1 H, $J_{9,10}$ = 8.2 Hz, H-10), 7.67 (dd, 1 H, $J_{7,9}$ = 1.8 Hz, H-9), 8.02 (d, 1 H, $J_{11,12}$ = 9.1 Hz, H-11), 8.12 (d, 1 H, H-3), 8.24 (d, 1 H, H-7), 8.30 (d, 1 H, H-12); ^{13}C NMR ($CDCl_3$) δ 15.29, 22.02, 28.59, 64.14, 69.87, 70.59, 73.09, 75.69, 101.75, 106.35, 115.06, 118.43, 119.48, 120.73, 122.40, 123.11, 126.17, 126.31, 127.20, 128.23, 128.54, 128.71, 128.89, 129.36, 131.10, 133.07, 134.98, 137.67, 145.32, 153.45, 160.83.

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Anal. Calcd for $C_{35}H_{32}O_6$: C, 76.6; H, 5.88. Found: C, 76.2; H, 5.76.

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Registry No. 1, 76231-50-0; 2, 65904-27-0; 3, 133009-70-8; 4, 133098-46-1; 5, 133098-47-2; 6, 133009-71-9; 7, 133009-72-0; 12, 122745-02-2; 12 isoproxy derivative, 133009-73-1; $Pd(OAc)_2$, 3375-31-3; 2-bromopropane, 75-26-3.

Ritter-like Reactions of 1,2-Anhydropyranose Derivatives

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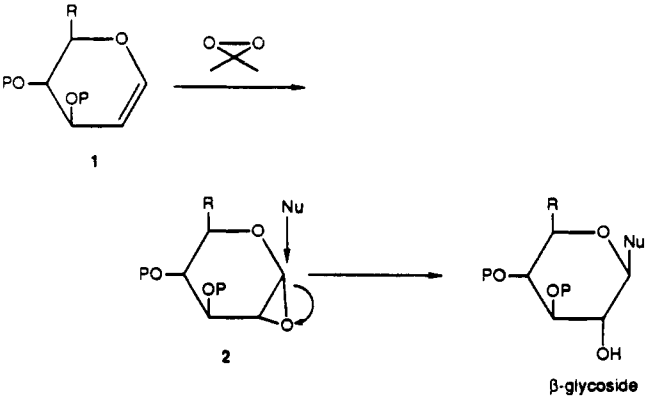
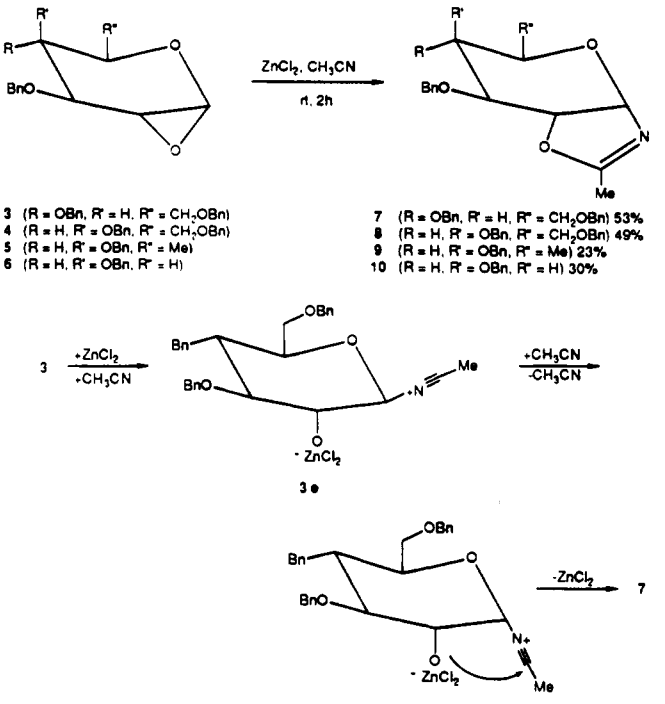
Recently we described a one step synthesis of α-1,2-anhydropyranose systems (cf. 2) from glycals (1).[1,2] If the resident protecting groups (P) lack participatory functionality (cf. benzyl or silyl ethers), nucleophilic attack occurs at the anomeric carbon with a high degree of stereoselectivity favoring inversion. Given the ease of reaching various glycals by total synthesis,[3] or by partial synthesis from other monosaccharides,[4] and given the excellent stereoselectivity which can be realized from the use of 1,2-anhydro sugars as glycosyl donors, the importance of the method is likely to grow. Application of such oxiranes to the synthesis of oligosaccharides and to the synthesis of other glycosyl donors (cf. *n*-pentenyl glycosides,[5] fluorides,[6] and thiophenyl ethers[7]) has recently been reported.[8] A potentially important outcome of the method is that it unveils a free hydroxyl group at C_2,[9] thus differentiating that oxygen from protected oxygens at carbons 3, 4, and 6. In this report we demonstrate an interesting application of this feature of the process in the context of the preparation of the previously uncharacterized C_1-nitrogen linked 1,2-glycooxazoline unit (see compounds 7–10)[10] by a Ritter[11] "type" solvolysis of these epoxides.[12]



Solutions of 1,2-anhydropyranose systems **3–6** in dry acetonitrile were treated with anhydrous zinc chloride to produce oxazolines **7–10** in the yields indicated. While the compounds were fully characterized (IR, ^1H NMR, HRMS, and optical rotation), they proved to be too sensitive for shipment and accurate combustion analysis. A pathway which is presumably general for the series is shown for the transformation of **3** → **7**. It is suggested that **3** undergoes the usual inversion to afford the equatorial anomeric system **3e**. This intermediate suffers inversion to produce axial anomer **3a**,[12] which is captured by the proximal α-hydroxyl function at C_2. Alternatively, **3e** might be produced by a S_Ni type opening of the oxirane.



With oxazoline **7** in hand, we tested the possibility of its intermediacy in the transformation of 2,3,4,6-tetra-*O*-benzyl-D-glucose to **11** and *N*-benzylacetamide under the

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