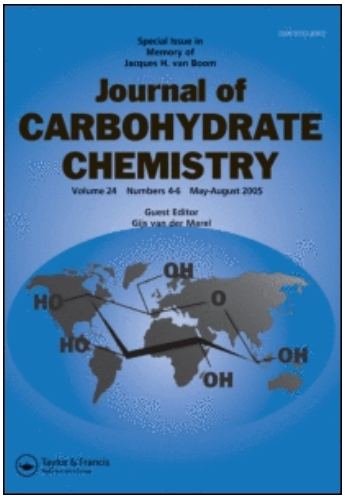

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Stereospecific C-Glycosdation Catalyzed by Pd(O)-Complexe

Mohamed Brakta[a]; Fabrice Le Borgne[a]; Denis Sinou[a]
[a] Laboratoire de Synthèse Asymétrique. U.A. CNRS n 463, Université Claude Bernard Lyon 1, Villeurbanne Cedex, France

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Communication

STEREOSPECIFIC C-GLYCOSIDATION CATALYZED BY Pd(O)-COMPLEXE

Mohamed BRAKTA, Fabrice LE BORGNE and Denis SINOU *

Laboratoire de Synthèse Asymétrique, U.A. CNRS n° 463

Université Claude Bernard Lyon I, 43 Bd du 11 Novembre 1918

69622 Villeurbanne Cedex - France.

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C-glyclosides are an important class of compounds receiving increasing attention recently[1-3]. One of the most important problems is the stereochemical control accompanying the formation of these compounds. Transition metal-mediated transformations, especially with Pd[4,5], generally show high stereochemical control. Several groups employed such methods for C-glycosidation: coupling of organomercury compounds with carbohydrate-derived enol ethers in the presence of $Pd(OAc)_2$[6], arylation of acetylated glycals catalyzed by $Pd(OAc)_2$[7], addition of some β -dicarbonyl compounds in the presence of $Pd(CH_3CN)_2Cl_2$ to various acylated glycals[8] and Pd(O)-catalyzed reaction of acetoxydihydropyran with tertiary carbanions like diethyl sodioformamidomalonate[9].

Although the apparent lack of reactivity of electron-rich allylic acetates having oxygen conjugation has been observed[10], an example of Pd(O)catalyzed addition of stabilized carbon nucleophiles to a trifluoroacetyl glucal, leading to C-glycoside, recently appeared in the

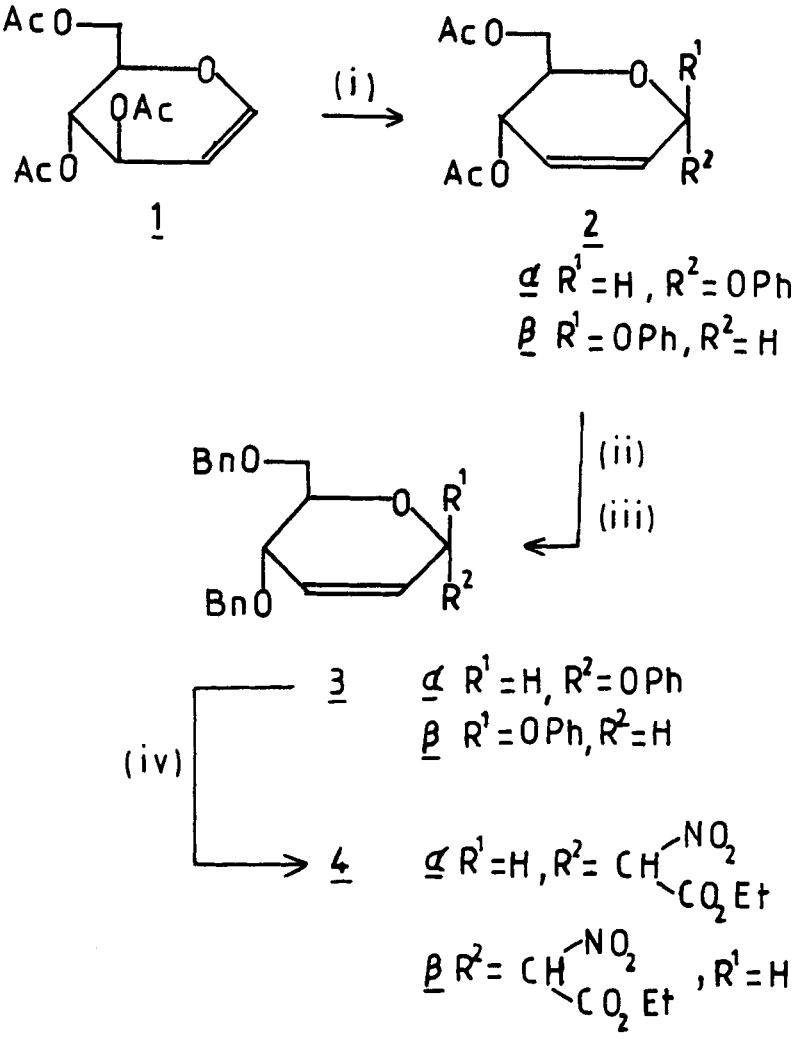
literature[11]. We wish to report our own results in this field using the Pd(0)catalyzed reaction.

Using the procedure of Ferrier[12], phenyl 4,6-di-O-acetyl-2,3-didehydro-2,3-dideoxy-D-erythro-hexoside **2** was obtained as an α : β mixture of 85:15 (yield = 77 %). Isolation of **2**α [mp 47-48°C, $[\alpha]_D^{20}$ + 165.5° (c 1.45: EtOH) and **2** β [oil, $[\alpha]_D^{20}$ + 72.5° (c 1.1: CH_2Cl_2)] by column chromatography [13,14], followed by deacetylation and benzylation of each anomer lead to compounds **3**α [oil, $[\alpha]_D^{20}$ + 43.7° (c 1.5: CH_2Cl_2)] and **3** β [oil, $[\alpha]_D^{20}$ + 32.9° (c 1.6: CH_2Cl_2)][13,15]. Compound **3**α or **3**β reacts with ethyl nitroacetate in the presence of 5 mol % bis (dibenzylidene acetone) Pd(0) and triphenylphosphine to give respectively (2-(4',6'-di-O-benzyl-2',3'-dideoxy-D-erythro-hex-2'-enopyranosyl) nitro ethyl ethanoate **4** α and **4** β in 70% and 50 % yield after purification[13,16] [**4** $[\alpha]_D^{20}$ + 65.4 (c 1.25: CH_2Cl_2): **4**β $[\alpha]_D^{20}$ + 81.8 (c 1.3: CH_2Cl_2)].

The reaction is regiospecific, alkylation occuring only at C-1'. Most important, the formation of **4** is also stereospecific with retention of configuration at C-1', as expected by the double inversion mechanism usually associated with this reaction[4,5]. At C-2, the reaction shows some stereoselectivity, the ratio of the two epimers being 75:25 and 60:40 respectively for **4** α and **4** β .

The high-field (350 MHz) ^1H NMR spectra of **4** α and **4** β are completely consistent with the assigned α - and β-configuration of the anomeric carbon. The coupling pattern $J_{4',5'}$ for the conformationally stable β-anomer with all groups in the quasi-equatorial or equatorial position is 9.4 Hz in **4** β , and for the conformationally equilibrated α-anomer 7.0 Hz in **4** α .This configuration was confirmed for **4** α by hydrogenation of the double bond leading to 2-(4',6'-di-O-benzyl-2',3'-dideoxy-α -D-erythro hexopyranosyl) nitro ethyl ethanoate showing a coupling pattern $J_{4'5'}$ of 5.5 consistent with a conformationally equilibrated anomer. They are in good agreement with previous examples of such assignments[17].

The scope and synthetic application of this method of glycosidation is under investigation.



(i) PhOH, PhCl, 140°C, 24h.; (ii) MeONa, MeOH, 25°C, 1h.; (iii) BnCl, KOH, DMSO, 24h.; (iv) $CH_2(NO_2)(COOEt)$, $Pd(dba)_2$, PPh_3, THF, 60°C.

Scheme

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13. Satisfactory analyses and spectral data were obtained for all new compounds.

14. Selected ^{1}H NMR data (80 MHz, $CDCl_3$, δ): **2** α : 7.4-6.9 (m, 5H, Ar), 6.0 (bs, 1H, H-2), 5.7 (bs, 1H, H-3), 5.4 (m, 1H,H-1), 4.3-4.0 (m, 4H,H-4, H-5, H-6), 2.2 (s, 3H,CH_3CO), 1.9 (s, 3H, CH_3CO). **2** β : 7.3-6.9 (m, 5H, Ar), 6.1 (bs, 1H,H-2), 5.75 (bs, 1H, H-3), 5.05 (bs, 1H, H-1), 4.3-4.0 (m, 4H, H-4, H-5, H-6), 2.1 (s, 3H, CH_3CO), 1.9 (s, 3H,CH_3CO).

15. Selected ^{1}H NMR data (350 MHz, $CDCl_3$, δ): **3**α : 7.4-7.0 (m, 15H, Ar), 6.21 (q, 1H, H-2,J_{23} = 10.4, J_{21} = 0), 5.91 (m, 1H, H-3, J_{31} = 2.4 J_{34} = 2.4), 5.71 (d,2H,H-1),4.64 and 4.58 (dd, 2H, CH_2O, J_{HH} = 11.6), 4.49 and 4.46 (dd,2H, CH_2O, J_{HH} = 11.6), 4.29 (dd, 1H, H-4, J_{45}=9.8), 4.08 (m, 1H, H-5, J_{56}=

3.7, $J_{56'}$=1.8), 3.75 (dd, 1H, H-6, $J_{66'}$=11), 3.67 (dd, 1H, H-6'). **3** β: 7.4-6.9 (m, 15H, Ar), 6.14 (ddd, 1H, H-3, J_{31}=1.1, J_{32}= 10.2, J_{34} = 3.6), 5.90 (ddd, 1H, H-2, J_{21}= 2.0, J_{24} = 1.2), 5.76 (ddd, 1H, H-1, J_{14}= 1.1), 4.58 (s, 2H, CH_2O), 4.47 (s, 2H,CH_2O), 4.19 (ddd, 1H, H-5 J_{54}= 4.6, J_{56}= 5.9, $J_{56'}$=5.6),4.01 (m, 1H, H-4), 3.73 (dd, 1H, H-6, $J_{66'}$=10.2), 3.64 (dd, 1H, H-6').

16. Selected ^{1}H NMR data (350 MHz, $CDCl_3$, δ): **4**α : 7.3-7.2 (m, 10H, Ar), 6.15 (m, 1H, H-3', $J_{3'1'}$= 2.0, $J_{3'2'}$= 10.4, $J_{3'4'}$=1.8), 5.88 m, 1H, H-2' $J_{2'1'}$= 1.8, $J_{2'4'}$= 1.8), 5.35 (d, 1H, H-2, $J_{21'}$= 5.35), 5.29 (d, 1H, H-2, $J_{21'}$ = 8.6), 5.02 and 5.01 (m, 1H,H- 1'), 4.61 and 4.45 (d, 2H,CH_2O, J_{HH}= 12.1), 4.59 and 4.46 (d, 2H, CH_2O, J_{HH}= 11.4), 4.32-4.22 (m, 2H, CH_2-CH_3), 4.17(dd, 1H, H-4', $J_{4'5'}$= 7.0), 3.74-3.60 (m, 3H,H-6', H-6",H-5'),1.28 and 1.25 (t, 3H, CH_3), **4** β: 7.47.2 (m, 10H, Ar), 6.12 (m,1H,H-3', $J_{3'2'}$= 10.4), 5.90 (ddd, 1H, H-2',$J_{2'3'}$= 9.9, $J_{2'1'}$= 1.7, $J_{2'4'}$ = 1.7) 5.85 (ddd,1H, H-2', $J_{2'3'}$= 10.4),5.35 (d, 1H, H-2,$J_{1'2}$= 5.4), 5.1 (d,1H, H-2, $J_{1'2}$= 8.9),5.03 and 4.96 (m, 1H, H1'), 4.62 (d, 1H, CH- Ar, J_{HH}= 10.7),4.56 (d, 1H, CH-Ar), 4.53 (d,1H, CH-Ar.J_{HH}=11.5) 4.45 (d, 1H,CH-Ar),4.14(q,2H.CH_2).3.98(q,2H.CH_2), 4.1 (dd, 1H, H-4', $J_{4'5'}$= 9.2), 3.95 (dd, 1H,H4', $J_{4'5'}$=9.2),3.83.5 (m, 3H, H-5', H-6', H-6"), 1.29 and 1.28 (t, 3H, CH_3).

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