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Synthesis of Polyfunctionalized Bis-Annulated Pyranosides: Useful Intermediates For Triquinane Synthesis

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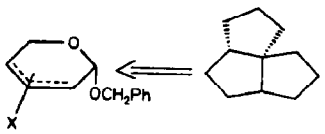
Abstract: A mild method for the synthesis of bis-cyclopentanoids on carbohydrate templates using the Pauson-Khand reaction is described.

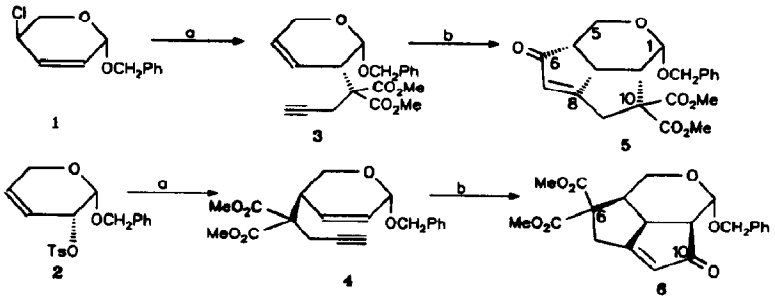
Due to their common occurrence in nature, bis-cyclopentanones are frequent and important targets for syntheses, either as final products or as potential intermediates for a wide variety of naturally occurring polyquinanes[1]. Therefore, different synthetic approaches were published recently[2]. Worth-while mentioning in this context is the elegant contributions from Fraser-Reid and co-workers[3] using carbohydrate precursors.

Recent studies in this laboratory have been concerned with the development of synthetic routes to chiral and polyfunctionalized hydrocarbons from carbohydrate precursors[4]. In the course of a research programme directed towards the synthesis of natural products, we want to present in this communication our preliminary results in building bis-annulated sugars via the Pauson-Khand reaction bearing the functional code required for triquinane syntheses[3] (Scheme 1).



Scheme 1

The starting materials 1 and 2 needed for the present study were prepared from easily accessible benzyl-2,3-anhydro-4-*O*-acetyl-α-D-ribopyranoside and benzyl-2-*O*-p-tosyl-3,4-anhydro-β-L-arabinopyranoside in 4 and 2 steps in 47%, respectively 66% overall yields[5,6]. The propargyl derivatives 3 and 4 were synthesized by the Pd-catalyzed[7] C-2 and C-4 alkylation of compounds 1 and 2 with the anion of dimethyl propargyl malonate in 76%, respectively 78% yields (Scheme 2).



Scheme 2. Reagents and condition: a) NaH/propargyl malonate, $Pd(PPh_3)_4$, THF, 0°C. b) $Co_2(CO)_8$/benzene, r.t.; DMSO, 50°C.

The propargyl derivatives **3** and **4** were converted quantitatively into the corresponding hexacarbonyl dicobalt complexes[8] which upon heating to 50°C for 24 h with a catalytic amount of DMSO afforded the polyfunctionalized products **5** and **6** in 75%, respectively 77% yields[9-11] (Scheme 2). The ^{1}H NMR spectra of **5** and **6** gave evidence that the bicyclic systems are cis-oriented which in turn indicates that the carbonylative acetylenic insertion always takes place from the same side where the propargylic moiety is located[10b,12] (**5**: $J_{1,2}$ = 3.4, $J_{2,3}$ = 7.1, $J_{3,4}$ = 7.6 Hz; **6**: $J_{1,2}$ = 7.9, $J_{2,3}$ = 6.6, $J_{3,4}$ = 6.4 Hz). The absolute stereochemistry of the cis-fused cyclopentanoides was also unambiguously assigned with the help of NOE experiments.

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9. (a) Compound **5**: m.p. 102-104°C; $[\alpha]_D$ +160.19 (c = 0.68, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.3-7.2 (m, 5H; Ar*H*), 5.60 (d, *J* = 1.5 Hz, 1H; *H*7), 4.70 (d, *J* = 12.0 Hz, 1H; OC*H*HPh), 4.60 (d, *J* = 3.4 Hz, 1H; *H*1), 4.50 (d, *J* = 11.9 Hz, 1H; OCH*H*Ph), 3.75 (dd, *J* = 11.7, 7.6 Hz, 1H; *H*5), 3.72 (s, 3H; OCH_3), 3.68 (s, 3H; OCH_3), 3.53 (d, *J* = 19.4 Hz, 1H; *H*9), 3.48 (m, 1H; *H*3), 3.28 (bdd, *J* = 10.1, 7.6 Hz, 1H; *H*4), 3.14 (dd, *J* = 19.4 Hz, 1H; *H*9'), 3.20 (dd, *J* = 11.7, 9.7 Hz, 1H; *H*5'), 2.78 (dd, *J* = 3.5, 7.1 Hz, 1H; *H*2); ^{13}C NMR (100 MHz, $CDCl_3$): 207.4 (*C*6), 183.7 (*C*8), 171.0, 168.9 (2xCO_2Me), 137.2-127.7 (*Ph*), 126.4 (*C*7), 97.0 (*C*1), 70.2 (OCH_2Ph), 65.7 (*C*10), 59.8 (*C*5), 53.3, 52.9 (2xOCH_3), 51.3 (*C*2), 46.8 (*C*4), 37.6 (*C*3), 34.3 (*C*9). (b) Compound **6**: oil; $[\alpha]_D$ -16.61 (c = 1.46, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.15-7.0 (m, 5H; Ar*H*), 5.79 (d, *J* = 1.5 Hz, 1H; *H*9), 4.90 (d, *J* = 7.9 Hz, 1H; *H*1), 4.34 (d, *J* =12.6 Hz, 1H; OC*H*HPh), 4.15 (d, *J* = 12.6 Hz, 1H; OCH*H*Ph), 3.59 (s, 3H; OCH_3), 3.51 (s, 3H; OCH_3), 3.38 (d, *J* = 20.3 Hz, 1H; *H*7), 3.13-3.20 (m, 2H; *H*4, *H*5), 3.10 (t, *J* = 12.0 Hz, 1H; *H*5'), 3.0 (t, *J* = 6.6 Hz, 1H; *H*3), 2.93 (d, *J* = 20.2 Hz, 1H; *H*7'), 2.9 (t, *J* = 7.3 Hz, 1H; *H*2); ^{13}C NMR (100 MHz, $CDCl_3$) : 206.8 (*C*10), 180.6 (*C*8), 171.3, 168.8 (2xCO_2Me), 137.2-127.1 (*Ph*) 126.0 (*C*9), 94.3 (*C*1), 69.4 (OCH_2Ph), 63.1 (*C*6) 53 5 (*C*5), 53 2, 52.9 (2xOCH_3), 49.8 (*C*2), 46.2 (*C*4), 38.9 (*C*3), 34.1 (*C*7).
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11. During the course of this work, two reports concerning the application of the Pauson-Khand reaction on sugar templates were appeared in the literature (see reference 10) .
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