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PALLADIUM-CATALYZED CARBONYL ALLYLATION OF ALDEHYDES BY ALLYLIC CYCLIC CARBONATES

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Abstract: Palladium(0)-catalyzed allylation of aldehydes by allylic cyclic carbonates with $SnCl_2$ proceeded smoothly to afford 1,3-diols with high diastereocontrol. For the exomethylene cyclic carbonate, allylation with aldehydes furnished 1,4-diols or 1,5-diols depending on amount of aldehydes.

Palladium(0)-catalyzed carbonyl allylation by allylic alcohols, acetates, and carbonates with SnCl₂ has been well documented by Y. Masuyama et al.¹ Recently, allylation of carbonyl compound by π - allylpalladium complex from allylic benzoate or ethers with diethylzinc was reported.² In connection with our programs to utilize allylic cyclic carbonates as substrates for Pd(0)-catalyzed reactions,³ we were interested in palladium(0)-catalyzed allylation of aldehydes with cyclic carbonates. Here we wish to report palladium(0)-catalyzed allylation by allylic cyclic carbonates to form *syn*-1,3-diols and mono- or diallylation of

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entry	Cabonate	Aldehyde	Time(h) ^a	Product	Yield(%) ^b
1	MPMO	РЪСНО	4	MPMO H H	91
2	la la	EtCHO	12	MPMO H H H	80
3	1a	C ₆ H ₁₁ CHO) 17	MPMO H H	85 H ₁₁
4 ^d	$= \underbrace{ \begin{array}{c} 0 \\ 0 \\ 2a \end{array}} = 0$	PhCHO	3	$= \underbrace{ \overset{\mathbf{3c}}{\overset{OH}{\overset{OH}{\overset{OH}{\overset{Ph}{\overset{Ph}}}}}}_{Ph}$	92
5 ^d	2a	EtCHO	3		70
6	2a	C ₆ H ₁₁ CHO	3	$\overset{\mathbf{4b}}{=} \overset{\mathrm{C}}{\overset{\mathrm{OH}}{\underset{C_6H_{11}}{\overset{\mathrm{OH}}{}}}}$	80
7 ^e	2a	PhCHO	4	$\overset{\mathbf{4c}}{=} \overset{OH}{\overset{Ph}{}}{P}}{\overset{Ph}{\overset{Ph}{}}}}{\overset{Ph}{\overset{Ph}{\overset{Ph}{}}{}}}}}}}}}}$	90
8 ^e	2a	EtCHO	5	Sa OH Et OH Et Sb	70

Table 1. Palladium-catalyzed carbonyl allylation of aldehydes

^a The carbonyl allylation of aldehydes (1 equiv) by allylic carbonates (2 equiv) with Pd(PhCN)₂Cl₂ (10 mol%) in the presence of SnCl₂·2H₂O (3 equiv) were run in DMI at 25°C ^b Isolated yield based on the aldehyde ^c The relative stereochemistry was determined by noe (¹H-NMR, 300 MHz)
 ^d Allylic cyclic carbonate : aldehyde : SnCl₂·2H₂O = 2 : 1 : 3 ^c Allylic cyclic carbonate : aldehyde

: $SnCl_2 \cdot 2H_2O = 1 : 1 : 3$

aldehydes by exomethylene cyclic carbonates to form 1,4- or 1,5-diols, respectively, by adjusting the amount of aldehydes.

The results of carbonyl allylation of aldehydes with chiral allylic carbonates are summarized in Table 1. The allylic cyclic carbonate 1^{3b} was reacted with one equiv of benzaldehyde in the presence of PdCl₂(PhCN)₂ catalyst(10 mol %) with SnCl₂·2H₂O(3 equiv) in DMI(1,3-dimethyl-2-imidazolidinone) as solvent at room temperature afforded 1,3-*syn*-diol **3a** as the sole product(entry 1). Instead of benzaldehyde, propionaldehyde and cyclohexylcarboxaldehyde were also used to prepare 1,3-diols **3b** and **3c** (entries 2 and 3). To establish the relative stereochemistry of the 1,2-*syn*-2,3,-*syn*-2-vinyl-1,3-diol **3a**, the compound **3a** was converted to the acetonide **6** and the relative stereochemistry was confirmed from the coupling constant⁴($J_{ab} = 2.5$ Hz, $J_{ac} = 2.4$ Hz) and noe experiments, which is shown in Scheme 1.



Scheme 1

Treatment of exomethylene cyclic carbonate 2^5 prepared from 2-methylene-1,3propanediol with 1 equiv of aldehydes and SnCl₂·2H₂O in the presence of Pd(0) catalyst provided 1,4-diols as the monoallylated products **4a-c**(entries 4-6). An interesting finding was that when **2** was treated with 2 equiv of benzaldehyde and propionaldehyde under the same conditions, the diallylation products, 1,5-diols **5a** and **5b** were obtained as the sole product, respectively(entries 7 and 8).

EXPERIMENTAL

(2*R*,3*S*,4*S*)-4-Phenyl-3-vinyl-1,2,4-butanetriol 1-*O*-*p*-methoxybenzylether(3a). To a stirred solution of 1a(50 mg, 0.19 mmol) and Pd(PhCN) $_2$ Cl $_2$ (8 mg, 10mol %) in DMI(0.3 mL) under N₂ atmosphere were successively added SnCl $_2$ ·2H₂O(66 mg, 0.29 mmol) and benzaldehyde(11 mg, 0.09 mmol). The resulting dark-brown solution was stirred at room temperature for 4 h, then the reaction mixture was extracted with ether. The organic layer was dried over anhydrous MgSO₄ and evaporated *in vacuo*. The crude product was separated by SiO₂ column chromatography(EtOAc/hexanes = 1 : 1 R_f = 0.46) to afford 3a(26 mg, 91%) [α]²⁵ -27.2 (*c* 1.3, CHCl₃). ¹H NMR (300 MHz, CDCl₃) δ 2.25 (m, 1H), 2.60 (bs, 1H), 2.90 (bs, 1H), 3.35 (m, 2H), 3.80 (s, 3H), 3.85 (m, 1H), 4.40 (s, 2H), 4.95 (m, 2H), 5.20 (dd, 1H, *J* = 10.3, 2.0 Hz), 6.0 (dt, 1H, *J* = 10.3, 2.0 Hz), 6.90 (d, 2H, *J* = 7.3 Hz) 7.20 (m, 7H). IR (neat); 3450, 3100, 2910, 2864, 1615, 1250 cm⁻¹. MS(m/e); 328(M⁺), 310, 222, 121(base peak), 107, 77.

(2R,3S,4R)-3-Vinyl-1,2,4-hexanetriol 1-O-p-methoxybenzylether(3b).

TLC; SiO₂, EtOAc/hexanes = 1 : 1, $R_f = 0.42$. $[\alpha]^{25}{}_{D} -4.0 (c \ 0.1, CHCl_3)$ ¹H NMR (300 MHz, CDCl₃) δ 0.85(t, 3H, J = 7.6 Hz), 1.40(q, 2H, J = 7.6 Hz), 2.05 (ddd, 1H, J = 9.9, 2.7 Hz), 2.80 (bs, 1H), 2.90 (bs, 1H), 3.35 (d, 2H, J = 6.0 Hz), 3.80 (s, 3H), 4.0 (m, 1H), 4.40 (s, 2H), 5.0 (m, 2H), 5.20 (dd, 1H, J = 10.3, 2.1 Hz), 5.90 (dt, 1H, J = 17.3, 10.1 Hz), 6.80 (d, 2H, J = 7.3 Hz) 7.20 (d, 2H, J = 7.3 Hz). IR (neat); 3407, 3055, 2956, 2858, 1650, 1260 cm⁻¹. MS(m/e); 281(M⁺+1), 280(M⁺), 264, 222, 121(base peak), 59.

(2R,3S,4R)-4-Cyclohexyl-3-Vinyl-1,2,4-butanetriol 1-O-p-methoxybenzylether

(3c). TLC; SiO₂, EtOAc/hexanes = 1 : 1, $R_f = 0.73$. $[\alpha]_D^{25}$ -7.1 (*c* 0.2, CHCl₃). ¹H NMR (300 MHz, CDCl₃) δ 1.10–1.30(m, 10H), 2.0(m, 1H), 2.30 (ddd, 1H J = 9.9, 2.7 Hz), 2.90 (bs, 1H), 3.0 (bs, 1H), 3.40 (d, 2H, J = 6.0 Hz), 3.80 (s, 3H), 4.05 (m, 1H), 4.45 (s, 2H), 4.50(m, 1H), 5.05 (dd, 1H, J = 18.6, 2.1Hz), 5.25 (dd, 1H, J = 11.5, 2.1 Hz), 6.0 (dt, 1H, J = 17.3, 10.1 Hz), 6.90 (d, 2H, J = 7.3 Hz) 7.20 (d, 2H, J = 7.3 Hz). IR (neat); 3424, 3055, 2910, 2864, 1612, 1248 cm⁻¹. MS(m/e); 334(M⁺), 220, 137, 121(base peak), 83.

(±)-2-Methylene-4-phenyl-1,4-butanediol(4a).

To a stirred solution of 2a(50 mg, 0.44 mmol) and $Pd(PhCN)_2Cl_2(16.8 \text{ mg}, 10 \text{mol} \%)$ in DMI(0.6 mL) under N₂ atmosphere were successively added $SnCl_2 \cdot 2H_2O(149 \text{ mg}, 0.66 \text{ mmol})$ and benzaldehyde(23.3 mg, 0.22 mmol). The resulting dark-brown solution was stirred at room temperature for 3h, then the reaction mixture was extracted with ether. The organic layer was dried over anhydrous MgSO₄ and evaporated *in vacuo*. The crude product was separated by SiO_2 column chromatography(EtOAc/hexanes = 1 : 1 R_f = 0.50) to afford 4a(36 mg, 92%). ¹H NMR (300 MHz, CDCl₃) δ 2.54(bs, 2H), 2.55 (d, 2H, *J* = 11.8 Hz), 4.10 (s, 2H), 4.85 (dd, 1H, *J* = 8.4, 4.5 Hz), 5.0 (s, 1H), 5.20 (s, 1H), 7.30 (m, 5H). IR (neat); 3300, 2960, 2850, 1650-1400, 1250 cm⁻¹. MS(m/e); 178(M⁺), 160, 107(base peak), 77.

(±)-2-Methylene-1,4-hexanediol(4b).

TLC; SiO₂, EtOAc/hexanes = 1 : 1 R_f = 0.35. ¹H NMR (300 MHz, CDCl₃) δ 0.95(t, 3H, J = 7.3 Hz), 1.50(q, 2H, J = 7.3 Hz), 2.25(bs, 2H), 2.35 (d, 2H, J = 11.9 Hz), 3.65 (m, 1H), 4.15 (s, 2H), 5.0 (s, 1H), 5.10 (s, 1H). IR (neat); 3350, 3060, 2963, 2840 cm⁻¹. MS(m/ e); 130(M⁺), 114(base peak), 113, 58.

(±)-2-Methylene-4-cyclohexyl-1,4-butanediol(4c).

TLC; SiO₂, EtOAc/hexanes = 1 : 1 R_f = 0.36. ¹H NMR (300 MHz, CDCl₃) δ 1.0–1.30(m, 10H), 2.10(m, 1H), 2.35 (bs, 1H), 2.40 (bs, 1H), 3.0 (d, 2H, J = 4.9 Hz), 3.50 (m, 1H), 4.10 (s, 2H), 5.0 (s, 1H), 5.15 (s, 1H). IR (neat); 3404, 3100, 2925, 2854 cm⁻¹. MS(m/ e); 184(M⁺), 101, 83, 57, 54(base peak).

(±)-3-Methylene-1,5-diphenylpentanediol(5a).

To a stirred solution of 2a(100 mg, 0.88 mmol) and Pd(PhCN)₂Cl₂(33.6 mg, 10 mol %) in DMI(1.2 mL) under N₂ atmosphere were successively added SnCl₂·2H₂O(496 mg, 2.64 mmol), and benzaldehyde(93 mg, 0.88 mmol). The resulting dark-brown solution was stirred at room temperature for 4h, then the reaction mixture was extracted with ether. The organic layer was dried over anhydrous MgSO₄ and evaporated *in vacuo*. The crude product was separated by SiO₂ column chromatography(EtOAc/ hexanes = 1 : 1 R_f = 0.68) to afford **5a**(212 mg, 90%) ¹H NMR (300 MHz, CDCl₃) δ 2.51(bs, 2H) 2.53 (d, 4H, *J* = 11.8 Hz), 4.90 (m, 2H), 5.10 (s, 1H), 5.15 (s, 1H),7.40 (m, 10H). IR (neat); 3387, 2936, 2871, 1650-1400, 1251 cm⁻¹. MS(m/e); 268(M⁺), 251, 250, 233, 232, 191, 161, 129(base peak), 107, 77.

(±)-5-Methylene-3,7-nonanediol(5b).

TLC; SiO₂, EtOAc/hexanes = 1 : 2 R_f = 0.19 ¹H NMR (300 MHz, CDCl₃) δ 0.95(t, 6H, J = 7.3 Hz), 1.50(q, 4H, J = 7.3 Hz), 2.25(bs, 2H), 2.30 (d, 4H, J = 11.9 Hz), 3.65 (m, 2H), 4.90 (s, 1H), 5.10 (s, 1H). IR (neat); 3350, 3060, 2963, 2840 cm⁻¹. MS(m/ e); 172(M⁺), 155, 127, 125(base peak), 112, 109.

(2R,3S,4S)-4-Phenyl-3-vinyl-2,5-isopropylidenedioxybutanol 1-O-p-methoxy-

benzylether(6). To a stirred solution of **3a**(50 mg, 0.15 mmol) in DMF under N₂ atmophere was added 0.1N HCl(2 drops) and 2-methoxypropene(0.03 mL, 0.30 mmol). After stirring at room temperature for 2 h, the reaction mixture was extracted with ether. The organic layer was dried over anhydrous MgSO₄ and evaporated *in vacuo*. The crude product was separated by SiO₂ column chromatography(EtOAc/hexanes = 1 : 7 R_f = 0.45) to afford **6**(44 mg, 90%). ¹H NMR (300 MHz, CDCl₃) δ 1.50–1.60 (bs, 6H), 2.38 (ddd, 1H, *J* = 9.9, 2.4 Hz), 3.35-3.50 (m, 2H), 3.80 (s, 3H), 4.40 (m, 1H), 4.50 (s, 2H), 4.70 (dd, 1H, *J* = 17.7, 2.2 Hz), 4.90 (dd, 1H, *J* = 10.4, 2.2 Hz), 5.15 (d, 1H, *J* = 2.5 Hz), 5.90 (dt, 1H, *J* = 17.3, 10.3 Hz), 6.90 (d, 2H, *J* = 7.3 Hz) 7.30 (m, 7H). IR (neat); 3100, 2910, 2864, 1615, 1250 cm⁻¹.

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