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Ni(II)-CATALYZED REGIO- AND DIASTEREOSELECTIVE ALLYLATION OF GRIGNARDS REAGENTS TO CHIRAL ALLYLIC CYCLIC CARBONATES

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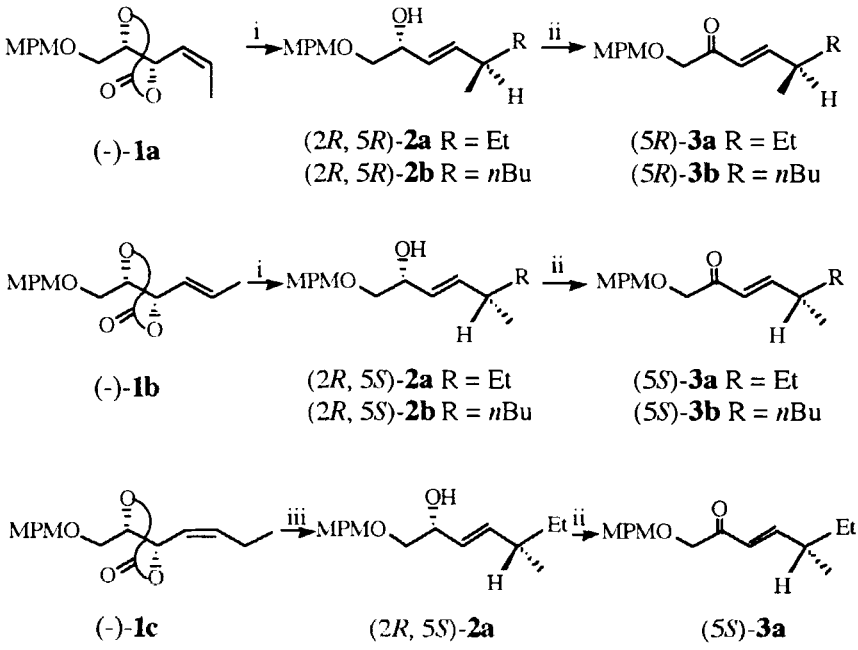
ABSTRACT: Reaction of chiral allylic cyclic carbonates with Grignards reagent in the presence of $NiCl_2$(dppe) as a catalyst afforded the alkylated (*E*)-allylic alcohols with high regio- and diastereoselectivity.

Recently, much attention has been paid to regio- and diastereoselective control in the coupling reactions of allylic systems with organometallics.[1] In the literature, alkylation of organomagnesium reagents with allylic alcohols, ethers, acetates, or halide in the presence of nickel complexes as catalyst.[2]

In connection with our research programs to prepare chiral synthons utilizing cyclic carbonates,[3] we have found that allylic cyclic carbonates are good substrates for excellent regio- and diastereoselective allylation reactions to form optically active (*E*)-allylic alcohols with Grignards reagents in the presence of $NiCl_2$(dppe) as catalyst.

The results of the reaction of the allylic cyclic carbonates **1a-c** with Grignards reagents and subsequent PCC oxidation of the resulting allylic alcohols are summarized in Scheme 1 and Table 1.



Scheme 1

Reagents and conditions: i) EtMgBr or *n*BuMgCl(4 equiv), $NiCl_2$(dppe)(5 mol %), THF, 0 °C→rt, 5 h ii) PCC, CH_2Cl_2, rt, 1 h iii) MeMgBr(4 equiv), $NiCl_2$(dppe) (5 mol %), THF, 0 °C→rt, 5 h.

Table 1. Ni(II)-Catalyzed or Organocuprate Induced Allylation of Allylic Cyclic Carbonates and PCC Oxidation of the Resulting Allylic Alcohols

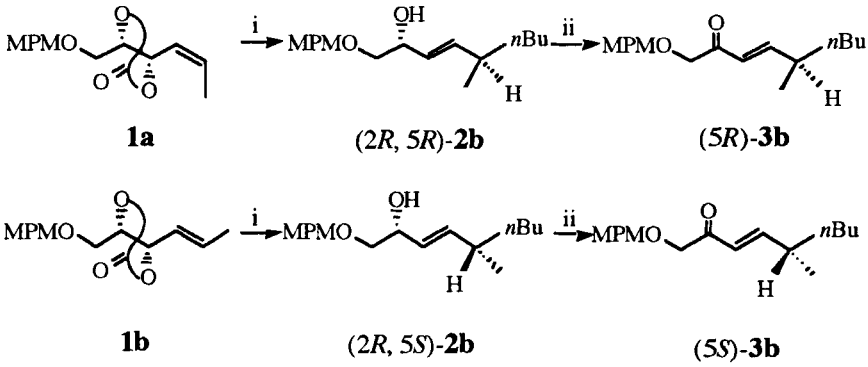
Entry	Substrate	Reagent[a]	Product[b,c]	Yield(%)	$[\alpha]^{25}_D$ (in $CHCl_3$)	Oxidation Product[d]	Yield(%)	$[\alpha]^{25}_D$ (in $CHCl_3$)
1	**1a**	EtMgBr(4), $NiCl_2$(dppe)(5 mol %)	(2*R*, 5*R*)-**2a**[e]	79	+7.7(*c* 0.9)	(5*R*)-**3a**	95	-14.8(*c* 0.1)
2	**1a**	*n*BuMgCl(4), $NiCl_2$(dppe)(5 mol %)	(2*R*, 5*R*)-**2b**	60	+6.7(*c* 0.3)	(5*R*)-**3b**	93	-14.2(*c* 0.3)
3	**1b**	EtMgBr(4), $NiCl_2$(dppe)(5 mol %)	(2*R*, 5*S*)-**2a**	80	+5.8(*c* 0.1)	(5*S*)-**3a**	95	+12.4(*c* 0.7)
4	**1b**	*n*BuMgCl(4), $NiCl_2$(dppe)(5 mol %)	(2*R*, 5*S*)-**2b**	58	+6.6(*c* 0.4)	(5*S*)-**3b**	91	+12.8(*c* 0.2)
5	**1c**	MeMgBr(4), $NiCl_2$(dppe)(5 mol %)	(2*R*, 5*S*)-**2a**	70	+5.6(*c* 0.1)	(5*S*)-**3a**	90	+10.7(*c* 0.1)
6	**1a**	nBuLi(10), CuCN(5) $BF_3{\cdot}OEt_2$(1)	(2*R*, 5*R*)-**2b**	82	+6.0(*c* 0.5)	(5*R*)-**3b**	96	-15.7(*c* 0.3)
7	**1b**	nBuLi(10), CuCN(5) $BF_3{\cdot}OEt_2$(1)	(2*R*, 5*S*)-**2b**	80	+6.6(*c* 0.1)	(5*S*)-**3b**	96	+16.0(*c* 0.7)

[a] Entries 1-5; RMgX(4 equiv), $NiCl_2$(dppe)(5 mol %), THF, 0 °C→ rt, 5 h. Entries 6-7; RLi(10 equiv), CuCN(5 equiv), $BF_3{\cdot}OEt_2$(1 equiv), -78 °C, THF, 30 min. [b] GC-MS analyses of the acetates were performated using Hewlett-Packard 5880 GC system [column: Ultra-2(5% phenyl, 12 m x 0.2 mm), oven temperature 180→280 °C, carrier gas N_2]. [c] Diastereoselectivity was confirmed by 300MHz ^{1}H NMR. [d] PCC, CH_2Cl_2, rt, 1 h. [e] The absolute configuration of the newly introduced stereogenic center of **2a** was correlated to the known (*S*)-(+)-4-methyl-1-hexanol (Mori, K; Suguro, T; Uchida, M. *Tetrahedron* **1978**, *34*, 3119) by (1) DDQ, CH_2Cl_2/ H_2O(18 : 1), 30 min(95%) (2) H_2, Rh/Al_2O_3, 1 atm(91%) (3) $NaIO_4$, Al_2O_3(88%) (4) $LiAlH_4$, ether(90%).

The (*Z*)-allylic cyclic carbonate **1a** was reacted with EtMgBr (4 equiv) in THF in the presence of $NiCl_2$(dppe) (5 mol %) to afford the (*E*)-allylic alcohol (2*R*, 5*R*)-**2a** with excellent diastereoselectivity (>99%) (entry 1). The diastereoselectivity was checked by 300 MHz ^{1}H NMR spectrum of (2*R*, 5*R*)-**2a** and GC-MS analysis of the acetate of (2*R*, 5*R*)-**2a**. The absolute configuration of the newly introduced stereogenic center at C-5 position of **2a** was correlated to the known (*S*)-(+)-4-methyl-1-hexanol.[4] The (*E*)-allylic alcohol (2*R*, 5*R*)-**2a** was oxidized to α, β-unsaturated ketone (5*R*)-**3a** (entry 1). Alternatively, the cyclic carbonate **1a** was also reacted with *n*-BuMgCl (4 equiv) in the presence of $NiCl_2$(dppe) as catalyst to provide (2*R*, 5*R*)-**2b**, which was oxidized to α, β-unsaturated ketone (5*R*)-**3b** (entry 2). This kind of chirality transfer was applied to (*E*)-allylic cyclic carbonate **1b**. The (*E*)-allylic cyclic carbonate **1b** with EtMgBr (4 equiv) gave (2*R*, 5*S*)-**2a** with the same diastereoselectivity (>99%) (entry 3). The compound (2*R*, 5*S*)-**2a** thus obtained was oxidized to α, β-unsaturated ketone (5*S*)-**3a**, of which the specific optical rotation was compared with that of (5*R*)-**3a**. This conversion was also applied to **1b** with *n*-BuMgCl (entry 4). Finally, ethyl substituted (*Z*)-allylic cyclic carbonate **1c** with MeMgBr (4 equiv) in the presence of $NiCl_2$(dppe) (5 mol %) afforded (2*R*, 5*S*)-**2a**, which is the other diastereoisomer of (2*R*, 5*S*)-**2a** (entry 5).

To compare and correlate the absolute configuration of the newly introduced stereogenic centers of (2*R*, 5*R*)-**2b** and (2*R*, 5*S*)-**2b**, the compounds (2*R*, 5*R*)-**2b** and (2*R*, 5*S*)-**2b** were prepared from the reactions of *cis* and *trans*-substituted allylic cyclic carbonates **1a** and **1b**, respectively, with higher order organocuprate $n Bu_2Cu(CN)Li_2$(Scheme 2).[3] The chemical shift for the methyl group of (2*R*, 5*R*)-**2b** thus prepared showed a doublet at δ 0.96,

whereas (2*R*, 5*S*)-**2b** showed at δ 0.97 in 300 MHz ^{1}H NMR. The diastereoisomers, (2*R*, 5*R*)-**2b** and (2*R*, 5*S*)-**2b**, were oxidized with PCC to afford the enantiomers (5*R*)-**3b** and (5*S*)-**3b**, respectively, and the values of the specific optical rotation were compared with each other (entries 6 and 7, Table 1).



Scheme 2

Reagents and conditions: i) *n*BuLi(10 equiv), CuCN(5 equiv), $BF_3{\cdot}OEt_2$(1 equiv), THF, -78 °C, 30 min ii) PCC, CH_2Cl_2, 1 h.

EXPERIMENTAL

General Procedures

(3*E*, 2*R*, 5*R*)-5-Methyl-3-hepten-1,2-diol 1-*O*-*p*-methoxybenzyl ether (2a): To a stirred solution of carbonate **1a** (100 mg, 0.35 mmol) and $NiCl_2$(dppe) (5 mol %) in dry THF (1 mL) at 0 °C under N_2 was added EtMgBr (0.61 mL, 4 equiv, 3 M in ether). After stirring for 5 h at room temperature, the reaction mixture was quenched with saturated NH_4Cl solution. THF was

evaporated and the residue was separated by SiO_2 column chromatography (EtOAc/hexanes = 1 : 2, R_f= 0.53) to afford (2*R*, 5*R*)-**2a** (70.6 mg, 79%). ^{1}H-NMR(300 MHz) δ 0.85 (t, 3H, *J* = 7.0 Hz), 0.96 (d, 3H, *J* = 6.7 Hz), 1.30 (m, 2H), 2.05 (m, 1H), 2.40 (bs, 1H), 3.35 (dd, 1H, *J* = 9.6, 8.4 Hz), 3.50 (dd, 1H, *J* = 9.6, 3.3 Hz), 3.80 (s, 3H), 4.30 (m, 1H), 4.50 (s, 2H), 5.37 (ddd, 1H, *J* = 15.5, 6.6, 1.1 Hz), 5.65 (ddd, 1H, *J* = 15.6, 7.5, 1.1 Hz), 6.90 (d, 2H, *J* = 8.7 Hz), 7.30 (d, 2H, *J* = 8.6 Hz). IR (neat) 3600, 3100, 2950, 2850, 1640, 1250 cm^{-1}. MS (m/e) 264 (M^+), 246, 137, 121 (base peak).

(3*E*, 5*R*)-5-methyl-1-*O*-*p*-methoxybenzyloxy-3-heptenone (3a): To a stirred solution of (2*R*, 5*R*)-**2a** (70 mg, 0.27 mmol) in CH_2Cl_2 (2 mL) at room temperature under N_2 atmosphere was added PCC (87.3 mg, 0.41 mmol). After stirring for 1 h, the reaction mixture was extracted with ether (15 mL). The ether layer was evaporated *in vacuo* and the crude product was separated by column chromatography (EtOAc/hexanes = 1 : 2, R_f = 0.60) to afford (3*E*, 5*R*)-**3a** (67.2 mg, 95%). ^{1}H-NMR(300 MHz) δ 0.87 (t, 3H, *J* = 8.0 Hz), 1.05 (d, 3H, *J* = 6.0 Hz), 1.40 (m, 2H), 2.20 (m, 1H), 3.82 (s, 3H), 4.20 (s, 2H), 4.55 (s, 2H), 6.25 (dd, 1H, *J* = 16.1, 1.3 Hz), 6.85 (d, 1H, *J* = 16.1 Hz), 6.90 (d, 2H, *J* = 8.7 Hz), 7.30 (d, 2H, *J* = 8.6 Hz). IR (neat) 2958, 2929, 2800, 1693, 1615, 1250 cm^{-1}. MS (m/e) 262(M^+), 138, 137, 126, 121(base peak).

(3*E*, 2*R*, 5*S*)-5-Methyl-3-hepten-1,2-diol 1-*O*-*p*-methoxybenzyl ether (2a): ^{1}H-NMR(300 MHz) δ 0.85 (t, 3H, *J* = 7.0 Hz), 0.97 (d, 3H, *J* = 6.7 Hz), 1.30 (m, 2H), 2.05 (m, 1H), 2.40 (bs, 1H), 3.35 (dd, 1H, *J* =9.6, 8.4 Hz), 3.50 (dd, 1H, *J* = 9.6, 3.3 Hz), 3.80 (s, 3H), 4.30 (m, 1H), 4.50 (s,

2H), 5.37 (ddd, 1H, J = 15.5, 6.6, 1.1 Hz), 5.65 (ddd, 1H, J = 15.6, 7.5, 1.1 Hz), 6.90 (d, 2H, J = 8.7 Hz), 7.30 (d, 2H, J = 8.6 Hz). IR (neat) 3600, 3100, 2950, 2850, 1640, 1250 cm^{-1}. MS (m/e) 264 (M^+), 246, 137, 121 (base peak).

(3*E*, 2*R*, 5*R*)-5-Methyl-3-nonen-1,2-diol 1-*O*-*p*-methoxybenzyl ether (2b): ^{1}H-NMR(300 MHz) δ 0.85 (t, 3H, J = 7.0 Hz), 0.96 (d, 3H, J = 6.8 Hz), 1.25 (m, 6H), 2.10 (m, 1H), 2.40 (bs, 1H), 3.35 (dd, 1H, J = 9.7, 8.5 Hz), 3.50 (dd, 1H, J = 9.6, 3.3 Hz), 3.80 (s, 3H), 4.30 (m, 1H), 4.50 (s, 2H), 5.37 (ddd, 1H, J = 15.5, 6.6, 1.1 Hz), 5.65 (ddd, 1H, J = 15.6, 7.5, 1.1 Hz), 6.90 (d, 2H, J = 8.7Hz), 7.30 (d, 2H, J = 8.6 Hz). IR (neat) 3600, 3100, 2950, 2850, 1640, 1250 cm^{-1}. MS (m/e) 292 (M^+), 275, 274, 137, 121 (base peak).

(3*E*, 2*R*, 5*S*)-5-Methyl-3-nonen-1,2-diol 1-*O*-*p*-methoxybenzyl ether (2b): ^{1}H-NMR(300 MHz) δ 0.85 (t, 3H, J = 7.0 Hz), 0.97 (d, 3H, J = 6.7 Hz), 1.25 (m, 6H), 2.10 (m, 1H), 2.40 (bs, 1H), 3.35 (dd, 1H, J = 9.7, 8.5 Hz), 3.50 (dd, 1H, J = 9.6, 3.3 Hz), 3.80 (s, 3H), 4.30 (m, 1H), 4.50 (s, 2H), 5.37 (ddd, 1H, J = 15.5, 6.6, 1.1 Hz), 5.65 (ddd, 1H, J = 15.6, 7.5, 1.1 Hz), 6.90 (d, 2H, J = 8.7 Hz), 7.30 (d, 2H, J = 8.6 Hz). IR (neat) 3600, 3100, 2950, 2850, 1640, 1250 cm^{-1}. MS (m/e) 292 (M^+), 275, 274, 137, 121 (base peak).

(3*E*, 5*S*)-5-methyl-1-*O*-*p*-methoxybenzyloxy-3-nonenone (3b): ^{1}H-NMR(300 MHz) δ 0.87 (t, 3H, J = 8.0 Hz), 1.05 (d, 3H, J = 6.0 Hz), 1.30 (m, 6H), 2.20 (m, 1H), 3.82 (s, 3H), 4.20 (s, 2H), 4.55 (s, 2H), 6.25 (dd,

1H, J = 16.1, 1.3 Hz), 6.85 (d, 1H, J = 16.1 Hz), 6.90 (d, 2H, J = 8.7 Hz), 7.30 (d, 2H, J = 8.6 Hz). IR (neat) 2958, 2929, 2800, 1693, 1615, 1250 cm^{-1}. MS (m/e) 290(M^+), 154, 137, 121(base peak).

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3. We have reported S_N2' addition of organocuprates to chiral allylic cyclic carbonates: see, Kang, S-K.; Lee, D-H.; Sim, H-S.; Lim, J-S. *Tetrahedron Lett.* **1993**, *34*, 91.
4. Mori, K.; Sugura, T.; Uchida, M. *Tetrahedron* **1978**, *34*, 3119.
5. The compound (-)-**1b**[$[\alpha]^{25}_D$ -60.0 (c 0.25)] was prepared from 4-*p*-methoxybenzyl-2, 3-*O*-isopropylidene-L-threose: (1) $Ph_3PCHCHO$, toluene, reflux, 30 min (87%) (2) $NaBH_4$, $CeCl_3 \cdot 7H_2O$, EtOH, rt, 1 h

(82%). (3) TsCl, Et_3N, DMAP, CH_2Cl_2, 0 °C, 30 min (4) $LiAlH_4$, THF, -30 °C → rt, 1 h (50% overall) (5) aq. HCl (10%), THF, 10 h (90%) (6) $CO(Im)_2$, CH_2Cl_2, rt, 30 min (87%).

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