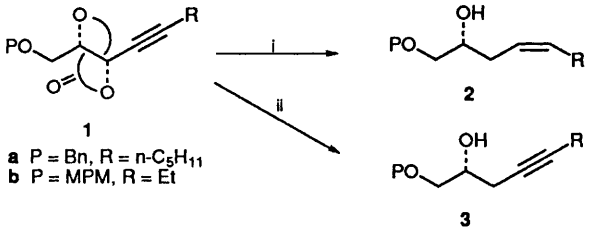
Synthesis of (*Z*)-Homoallylic Alcohols and Homoprop-2-ynylic Alcohols *via* Palladium-catalysed Hydrogenolysis of Prop-2-ynylic Cyclic Carbonates

Suk-Ku Kang,* Dong-Chul Park, Dong-Gyu Cho, Jea-Uk Chung and Kyung-Yun Jung
Department of Chemistry, Sung Kyun Kwan University, Natural Science Campus, Suwon 440-746, Korea

The decarboxylation–hydrogenolysis of prop-2-ynylic cyclic carbonates which have an internal acetylenic bond with ammonium formate in the presence of a catalytic amount of [Pd(acac)$_2$] and Bu$^n_3$P afforded (*Z*)-homoallylic alcohols or homoprop-2-ynylic alcohols depending on the reaction conditions, however, hydrogenolysis of terminal prop-2-ynylic cyclic carbonates gave homoallylic alcohols; using (*Z*)-homoallylic alcohol **2b** as a chiral synthon, the male sex pheromone of the pyralid moth *Aphomia gularis* has been synthesized.

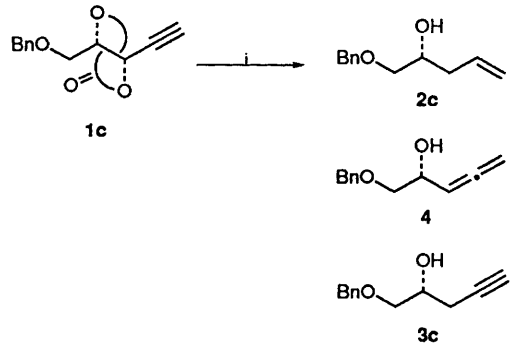
Optically active (*Z*)-homoallylic and homoprop-2-ynylic alcohols are versatile chiral synthons in organic synthesis. In the literature, stereoselective synthesis of (*Z*)-homoallylic alcohols by addition of crotylstannanes to aromatic aldehydes has been reported.[1] We report here a convenient one-pot synthetic method for the highly stereoselective preparation of (*Z*)-homoallylic alcohols **2** and homoprop-2-ynylic alcohols **3** utilizing palladium-catalysed selective hydrogenolysis,[2,3] details of which are shown in Scheme 1 and Table 1.



Scheme 1 *Reagents and conditions:* i, HCO_2NH_4 (4 equiv.), [Pd(acac)$_2$]–Bu$^n_3$P (cat.), PhH, reflux; ii, HCO_2NH_4 (1 equiv.), [Pd(acac)$_2$]–Bu$^n_3$P (cat.), PhH, room temp. (MPM = *p*-methoxyphenylmethyl)

The internal prop-2-ynylic cyclic carbonate **1a** reacted with 4 equiv. of ammonium formate in the presence of [Pd(acac)$_2$] (acac = acetylacetonate) and Bu$^n_3$P as catalysts in benzene at reflux for 3 h to afford the (*Z*)-homoallylic alcohol **2a** in 76% yield, the structure of which was confirmed by ^{1}H NMR (300 MHz) coupling constants of the olefinic protons (entry 1). It is presumed that Pd-catalysed decarboxylation–hydrogenolysis gives the homoprop-2-ynylic alcohol **3a** as an intermediate (checked by TLC), which is subsequently reduced with excellent stereoselectivity (> 99%) to the (*Z*)-homoallylic alcohol **2a** by ammonium formate as a hydrogen donor in the presence of Pd-catalyst.[4] As indirect evidence for the intermediary of alcohol **3a**, the reaction of the carbonate **1a** with 1 equiv. of [Pd(acac)$_2$] and Bu$^n_3$P afforded the homoprop-2-ynylic alcohol **3a** in 93% yield (entry 2).† It is notable that under the same conditions, with benzene as solvent, stirring at room temperature afforded **3a** in 97% yield (entry 3). This conversion was applied to the prop-2-ynylic cyclic carbonate **1b** and thus the (*Z*)-homoallylic alcohol **2b** and the homoprop-2-ynylic alcohol **3b** were obtained (entries 4 and 5).

In contrast to the internal prop-2-ynylic cyclic carbonate, decarboxylation–hydrogenolysis of the terminal prop-2-ynylic carbonate **1c**,[5] with 2 equiv. of ammonium formate in the presence of a catalytic amount of [Pd(acac)$_2$] and Bu$^n_3$P in tetrahydrofuran (THF) at reflux for 30 min, provided the homoallylic alcohol **2c** as the sole product (entry 6).‡ Presumably, the allenic alcohol **4** and the homoprop-2-ynylic alcohol **3c** are the intermediates. As indirect evidence for this, treatment of **1c** with 1 equiv. of ammonium formate in the presence of [Pd(acac)$_2$] and Bu$^n_3$P in THF at reflux provided mixtures of the allenic alcohol **4** and the homoprop-2-ynylic alcohol **3c** (Scheme 2; entry 7).§ It is notable that the reaction of



Scheme 2 *Reagents and conditions:* i, HCO_2NH_4 (1 equiv.), [Pd(acac)$_2$]–Bu$^n_3$P (cat.), THF, reflux, 30 min

1c with 1 equiv. of ammonium formate in the presence of [Pd(acac)$_2$] and Bu$^n_3$P in benzene at room temperature afforded the allenic alcohol **4** as the major product (entry 8).

The results of the palladium-catalysed hydrogenolysis of prop-2-ynylic cyclic carbonates are summarized in Table 1.

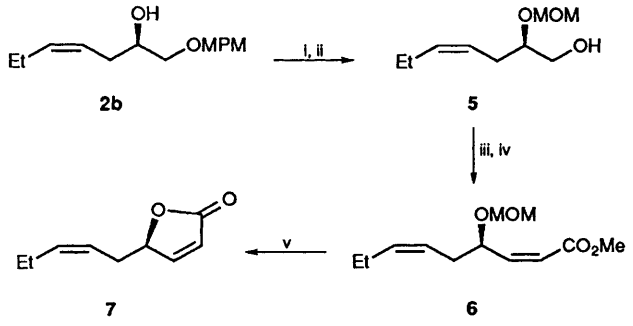
Using (*Z*)-homoallylic alcohol **2b** as a chiral synthon, the male sex pheromone of the pyralid moth *Aphomia gularis* **7**[6] was synthesized (Scheme 3). The homoallylic alcohol **2b** was protected as methoxymethyl (MOM) ether and then the *p*-methoxyphenylmethyl (MPM) protecting group was removed to furnish the alcohol **5**, $[\alpha]_D^{25}$ −24 (*c* 0.46, $CHCl_3$). The alcohol **5** was oxidized and Wittig olefination gave the α,β-unsaturated ester **6** (*Z*:*E* = 1.3:1). The (*Z*)-α,β-unsaturated ester **6** was subjected to deprotection, followed by lactonization

† [Pd$_2$(dba)$_3$]·$CHCl_3$ (5 mol%) can be used instead of [Pd(acac)$_2$].
‡ In our hands, using [Pd(PPh$_3$)$_4$] (5 mol%) in THF at reflux did not furnish the product. However, with [Pd(PPh$_3$)$_4$] in MeCN at reflux for 40 min, the product **2c** was obtained in 79% yield.
§ Treatment of **1c** with [Pd$_2$(dba)$_3$]·$CHCl_3$ (5 mol%), Bu$^n_3$P (5 mol%), HCO_2NH_4 (1 equiv.) in THF at reflux for 30 min gave **4** and **3c** in a ratio of 1:2.4. Under the same conditions, with 2 equiv. of HCO_2NH_4, the reaction of **1c** gave the homoallylic alcohol **2c** in 73% yield.

Table 1 Pd^0-Catalysed hydrogenolysis of prop-2-ynylic cyclic carbonates

Entry	Substrate	HCO_2NH_4 (mol)	Solvent	Conditions[a] Temp. (°C)	Time (h)	Product[b]	Yield (%)[d]
1	**1a**	4	Benzene	80	3	**2a**	76
2	**1a**	1	THF	65	0.5	**3a**	93
3	**1a**	1	Benzene	25	2	**3a**	97
4	**1b**	4	Benzene	80	3	**2b**[c]	74
5	**1b**	1	Benzene	80	0.2	**3b**	86
6	**1c**	2	THF	65	0.5	**2c**	82
7	**1c**	1	THF	65	0.5	**4** + **3c** (1:1)	93
8	**1c**	1	Benzene	25	2	**4** + **3c** (5.92:1)	97

[a] All the reactions were run in the presence of [Pd(acac)$_2$] (5 mol%) and $Bu^n{}_3P$ (5 mol%). [b] $[\alpha]_D^{25}$ Values in $CHCl_3$: **2a**, −4.4 (*c* 4.6); **3a**, −10.7 (*c* 1.5); **2b**, −2.4 (*c* 2.3); **3b**, −8.0 (*c* 3.0); **2c**, −6.6 (*c* 2.1). [b] The selectivity was checked by GLC analysis of the acetate of **2b** using a Hewlett-Packard 5880 GC system [column: ultra-2 (5% pheugl), 0.2 × 12 m oven temp. 180–280 °C, carrier gas. He 0.6 cm^3 min^{-1}. The retention time of the acetate of **2b** was 7.15 min. [d] Yields are isolated yields.



Scheme 3 *Reagents and conditions:* i, MOMCl, $Pr^i{}_2NEt$, 0 °C ⟶ room temp., 2 h (85%); ii, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), CH_2Cl_2, H_2O (18 : 1), 30 min (96%); iii, $(COCl)_2$, dimethyl sulfoxide (DMSO), Et_3N, CH_2Cl_2, −78 °C; iv, Ph_3PCHCO_2Me, MeOH, 0 °C, 5 h (30% overall); v, trifluoroacetic acid (TFA), CH_2Cl_2–H_2O (10 : 1) (80%)

to afford (4*R*,2*Z*,6*Z*)-nona-2,6-dien-4-olide, **7**, $[\alpha]_D^{25}$ −160 (*c* 0.2, $CHCl_3$) {lit.,[6] $[\alpha]_D^{25}$ −162 (*c* 0.650, $CHCl_3$)}.*

Experimental

Typical Procedures.—Preparation of **2a**. [Pd(acac)$_2$] and $Bu^n{}_3P$ (5 mol%) were mixed in a 1 : 1 ratio in dry benzene (5 cm^3) to form a pale yellow solution. Then prop-2-ynylic cyclic carbonate **1a** (303 mg, 1.00 mmol) in dry benzene (5 cm^3) was added followed by ammonium formate (2.52 mg, 4.0 mmol) and the mixture was stirred for 3 h at reflux. The benzene was evaporated and then the residue was separated by SiO_2 column chromatography (EtOAc–hexanes, 1 : 3, R_f 0.60) to afford alcohol **2a** (199 mg, 76%), $[\alpha]_D^{25}$† −4.4 (*c* 4.6, $CHCl_3$); δ_H(300 MHz; $CDCl_3$‡) 0.90 (3 H, t, *J* 7.0), 1.30 (6 H, m), 2.05 (2 H, m), 2.26 (2 H, m), 3.34 (1 H, m), 3.50 (1 H, m), 3.85 (1 H, m), 4.55 (2 H, s), 5.37 (1 H, dt, *J* 11 and 7.3), 5.48 (1 H, dt, *J* 11 and 7.3), 7.32 (5 H, s); ν_{max}(neat)/cm^{-1} 3400 and 1620; *m*/*z* 262 (M^+) and 91 (base peak) (Found: C, 77.5; H, 10.0. $C_{17}H_{26}O_2$ requires C, 77.86; H, 9.92%).

Preparation of **3a**. [Pd(acac)$_2$] and $Bu^n{}_3P$ (5 mol%) were mixed in a 1 : 1 ratio in dry benzene (5 cm^3) to form a pale yellow solution. Then prop-2-ynylic cyclic carbonate **1a** (303 mg, 1.00 mmol) in dry benzene (5 cm^3) was added followed by ammonium formate (63 mg, 1.0 mmol) and the mixture was stirred for 2 h at room temperature. The THF was evaporated and the residue was separated by SiO_2 column chromatography (EtOAc–hexanes, 1 : 4, R_f 0.56) to afford alcohol **3a** (252 mg, 97%), $[\alpha]_D^{25}$ −10.7 (*c* 1.5, $CHCl_3$); δ_H(300 MHz; $CDCl_3$) 0.90 (3 H, t, *J* 7.1), 1.32 (4 H, m), 1.47 (2 H, m), 2.15 (2 H, m), 2.43 (2 H, m), 3.50 (1 H, dd, *J* 9.6 and 6.7), 3.61 (1 H, dd, *J* 9.6 and 4.0), 3.93 (1 H, m), 4.58 (2 H, s) and 7.34 (5 H, s); *m*/*z* 260 (M^+), 189 (19%), 91 (base peak) and 79 (11) (Found: C, 78.15; H, 9.3. $C_{17}H_{24}O$ requires C, 78.46; H, 9.23).

Acknowledgements

Generous financial support by the Korea Science and Engineering Foundation (KOSEF)–the Organic Chemistry Research Center (OCRC) is gratefully acknowledged.

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Paper 3/06391G
Received 26*th October* 1993
Accepted 30*th November* 1993

* **7**: δ_H(300 MHz, $CDCl_3$) 0.96 (3 H, t, *J* 7), 2.04 (2 H, m), 2.50 (2 H, m), 5.09 (1 H, m), 5.36 (1 H, m), 5.60 (1 H, m), 6.14 (1 H, dd, *J* 6 and 2.1) and 7.45 (1 H, dd, *J* 6 and 1.6); ν_{max}(neat)/cm^{-1} 2950, 2926, 2850, 1755, 1450, 1250, 1240, 1160, 1100, 830, 740 and 700.
† $[\alpha]_D$ Values are given in units of 10^{-1} deg cm^2 g^{-1}.
‡ *J* Values are given in Hz.