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Pd(0)-CATALYZED ELIMINATION AND COUPLING OF ALLYLIC CYCLIC CARBONATES

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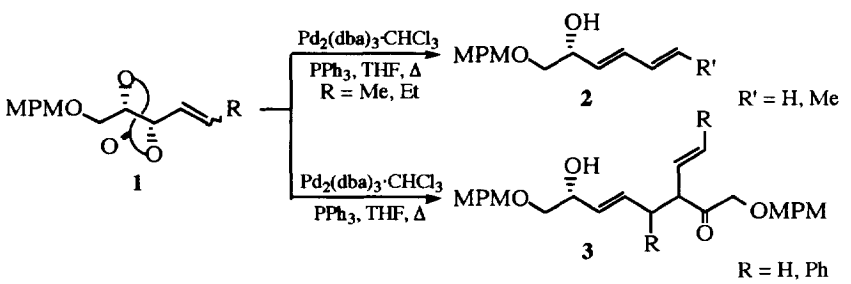
Abstract: The alkyl substituted allylic cyclic carbonates **1a-d** undergo elimination by using a catalytic amount of Pd(0) complex to form dienols **2a-b**. However, on treatment of the unsubstituted or phenyl substituted allylic cyclic carbonates **1e** and **1f** with palladium(0) catalyst, deprotonation-elimination of π-allylpalladium complex followed by condensation with the other π-allylpalladium complex provided the coupled products **3a** and **3b**, respectively.

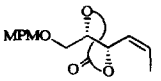
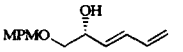
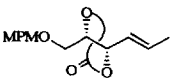
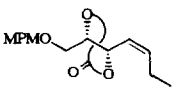
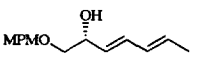
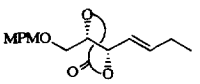
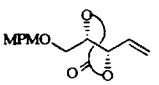
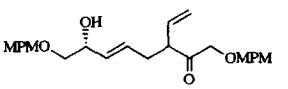
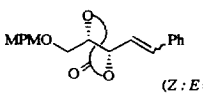
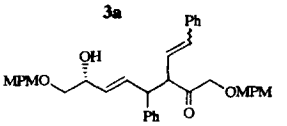
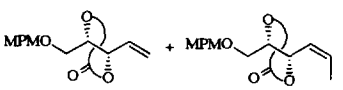
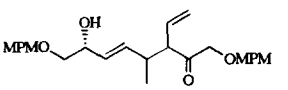
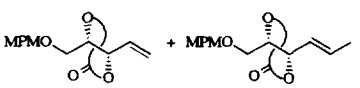
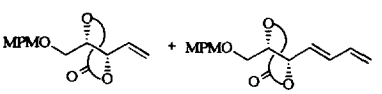
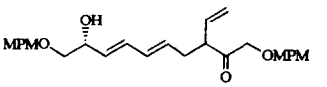
Chiral 2, 4-dienols are versatile Diels-Alder dienes in organic synthesis. As our program to utilize allylic cyclic carbonates *via* a π-allylpalladium complex in preparing useful chiral synthons,[1] we have found that 2, 4-dienols can be prepared from the alkyl substituted allylic cyclic carbonates utilizing palladium-catalyzed elimination reaction.[2] However, treatment of the unsubstituted or phenyl substituted allylic cyclic carbonates under the same conditions resulted in the formation of unusual coupled products, which are shown in Scheme 1.



Scheme 1

The results of Pd(0)-catalyzed elimination and elimination-coupling are summarized in Table 1. The methyl substituted allylic cyclic carbonate **1a** and **1b** were reacted with a catalytic amount of $Pd_2(dba)_3{\cdot}CHCl_3$ (5 mol %) and triphenylphosphine (20 mol %) in refluxing THF for 15 min to afford 2, 4-dienol **2a**[3] (entries 1 and 2). This elimination can be explained *via* the formation of π-allylpalladium complex followed by deprotonation-elimination to regenerate Pd(0)

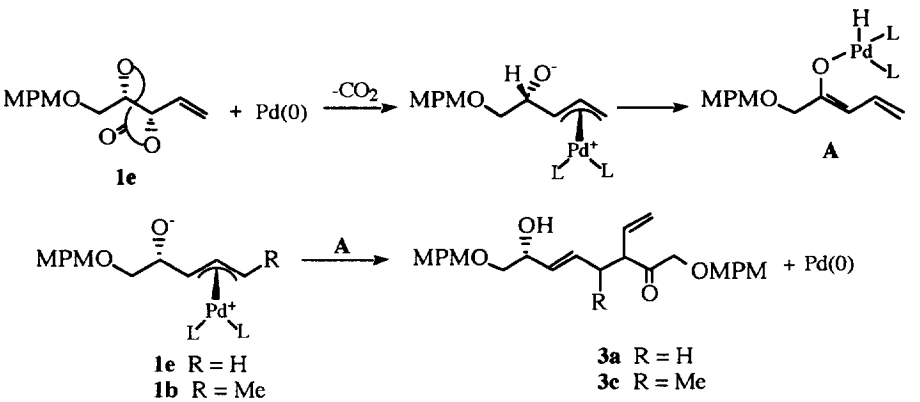
Table1. Pd(0)- Catalyzed Elimination and Coupling of Allylic Cyclic Carbonates[a]

Entry	Substrate[b]	Product	Isolated Yield (%)
1	 **1a**	 **2a**[c]	93
2	 **1b**	**2a**	91
3	 **1c**	 **2b**[d] (*E* : Z = 12 : 1)	89
4	 **1d**	**2b** (*E* : Z = 12 : 1)	85
5	 **1e**	 **3a**	91
6	 (Z : E = 6 : 1) **1f**	 **3b**	90
7	 **1e** **1a**	 **3c**[6]	75
8	 **1e** **1b**	**3c**[6]	80
9	 **1e** **1g**	 **3d**	70

[a] All the reactions were run with the substrate(1 equiv) and $Pd_2(dba)_3 \cdot CHCl_3$ (5 mol %) and Ph_3P(20 mol %) [b] MPM = Methoxyphenylmethyl

[c] $[\alpha]^{25}_D$ -33.0 (*c* 0.3, $CHCl_3$) [d] $[\alpha]^{25}_D$ -11.0 (*c* 0.5, $CHCl_3$)

species. It is noteworthy that (*Z*)-and (*E*)-ethyl substituted allylic carbonates **1c**[4] and **1d**[4] afford identical product **2b**.[3] The ratio of (*E*)- and (*Z*)-isomers for the methyl group of the compound **2b** at C(6) was *ca* 12 : 1 checked by GC-MS (entries 3 and 4).[5] It is presumed that in these elimination equilibration of π- and σ-complexes must be faster than elimination of the proton in the π–allylpalladium complex. In contrast to the above cases, when the allylic cyclic carbonate **1e** was subjected to reflux with a catalytic amount of $Pd_2(dba)_3{\cdot}CHCl_3$ and triphenylphosphine, the dimerized compound **3a** was obtained in 91% yield (entry 4). The formation of **3a** could be rationalized *via* a π-allylpalladium complex, which was eliminated to give a unusual enolate. The enolate thus formed as a nucleophile was subjected to allylic substution with the π-allyl complex of allylic cyclic carbonate **1e** to form the coupled product **3a** and the liberated Pd(0) maintained in the catalytic cycle (Scheme 2). Similarly, the phenyl substituted cyclic carbonate **1f** provided **3b**[3] under the same conditions (entry 6). An interesting finding was that when **1e** was treated with **1a** or **1b** in THF under the same conditions, the cross-coupled adduct **3c**[3,6] was obtained as a sole product in high yields without any incidental formation of **2a** (entries 7 and 8)(Scheme 2). The reaction of **1e** and dienylic cyclic carbonate **1g** together afforded ε-substituted allylic alcohol **3d** in 70% yield (entry 9).



Scheme 2

The typical procedure is as follows. Preparation of **2a**: To a stirred solution of $Pd_2(dba)_3{\cdot}CHCl_3$ (42 mg, 5 mol %) and Ph_3P (42 mg, 20 mol %) in dry THF(1 mL) was added **1a** (222 mg, 0.40 mmol) in dry THF(1 mL). After stirring at reflux for 15 min, the reaction mixture was cooled and THF was evaporated. The residue was separated by SiO_2 column chromatography (EtOAc/hexanes 1 : 1, R_f = 0.61) to afford **2a** (174 mg, 93%).

In summary, we have developed an efficient route to optically pure (*E*, *E*)-2,4-dienols by Pd(0)-catalyzed elimination of the alkyl substituted allylic cyclic carbonates. Further studies on mechanistic aspects including stereochemical courses in the coupling reaction is in progress.

Acknowledgment. Generous financial support by KOSEF-OCRC and Ministry of Education(BSRI-94-3420) is gratefully acknowledged.

References and Notes

1. (a) Kang, S-K.; Kim, S-G.; Lee, J-S. *Tetrahedron: Asymmetry* **1992**, *3*, 1139. (b) Kang, S-K.; Park, D -C.; Cho, D-G.; Chung, J-U.; Jung, K-Y. *J. Chem. Soc. Perkin Trans I.* **1994**. 237. (c) Kang, S-K.; Park, D-C.; Jeon, J-H.; Rho, H-S.; Yu, C-M. *Tetrahedron Lett.* **1994**, *35*, 2357. (d) Kang, S-K.; Park, D-C.; Rho, H-S.; Yu, C-M.; Hong, J-H. *Synth. Commun.*, in press.
2. Elimination of allylic acetates has been known: Tsuji, J.; Yamakawa, T.; Kaito, M.; Mandai, T. *Tetrahedron Lett.* **1978**, *24*, 2075.
3. Satisfactory spectral and physical data were obtained for all new compounds and are in accord with the assigned structure. Selected data are as follows. **2a**: TLC, SiO_2, EtOAc/hexanes 1 : 1, R_f = 0.61. ^1H NMR(300 MHz, $CDCl_3$) δ 2.50(bs, 1H), 3.35(dd, 1H, *J* = 16.5, 8.15 Hz), 3.50(dd, 1H, *J* = 9.6, 3.4 Hz), 3.80(s, 3H), 4.40(m,1H), 4.50(s, 2H), 5.10(d, 1H, *J* = 9.0 Hz), 5.20(d, 1H, *J* = 16 Hz), 5.70(dd, 1H, *J* = 14.5, 6.1 Hz), 6.30(m, 2H), 6.90(d, 2H, *J* = 7.3 Hz), 7.25(d, 2H, *J* = 7.3 Hz). IR(neat) 3500, 2959, 2863, 1610, 1246 cm^{-1}. MS(m/e) 235(M^++1), 234(M^+) 121(base peak). $[\alpha]^{25}_D$ = -34.2 (*c* 0.5, $CHCl_3$). **2b**: TLC, SiO_2, EtOAc/ hexanes 1 : 2, R_f = 0.50. ^1H NMR(300 MHz, $CDCl_3$) δ 1.75(d, 3H, *J* = 7.0 Hz), 2.50(d, 1H, *J* = 3.1 Hz), 3.40(m, 1H), 3.50(m, 1H), 3.80(s, 3H), 4.40(m,1H), 4.50(s, 2H), 5.40-5.80(m, 2H), 6.0(m, 1H), 6.30(dd, 0.5H, *J* = 15.2, 10.3 Hz), 6.65(dd, 0.5H, *J* = 15.2, 10.3 Hz), 6.90(d, 2H, *J* = 7.3 Hz), 7.25(d, 2H, *J* = 7.3 Hz). IR(neat) 3550, 2959, 2863, 1611, 1248 cm^{-1}. MS(m/e) 248(M^+), 137, 121(base peak). $[\alpha]^{25}_D$ = -11.0 (*c* 0.5, $CHCl_3$). **3a**: TLC; SiO_2, EtOAc/hexanes 1 : 1, R_f = 0.35. ^1H NMR(300 MHz, $CDCl_3$) δ 2.25(m, 1H), 2.35(bs, 1H), 2.50(m, 1H), 3.30(m, 2H), 3.45(dd, 1H, *J* = 9.6, 3.4 Hz), 3.80(s, 6H), 4.10(d, 2H, *J* = 4.6 Hz), 4.25(m, 1H), 4.48, 4.49(s, 4H), 5.15(dd, 2H, *J* = 15.6, 10.8 Hz), 5.45(ddd, 1H, *J* = 15.5, 6.1, 1.4 Hz), 5.70(m, 2H), 6.90(d, 4H, *J* = 7.3 Hz), 7.30(d, 4H, *J* = 7.3 Hz). IR(neat) 3417, 2956, 2858, 1722, 1610, 1246 cm^{-1}. MS(m/e) 440(M^+), 121(base peak). **3b**: TLC, SiO_2, EtOAc/hexanes 1 : 2, R_f = 0.19. ^1H NMR(300 MHz, $CDCl_3$) δ 2.30(bs, 1H), 3.25(dd, 1H, *J* = 9.4, 8.07 Hz), 3.45(dd, 1H, *J* = 9.5, 3.4 Hz), 3.80(s, 6H), 3.90(m, 2H), 4.10(d, 2H, *J* = 4.6 Hz), 4.25(m, 1H), 4.41, 4.47(s, 4H), 5.50(dd, 1H, *J* = 15.2, 5.2 Hz), 5.85(dd, 1H, *J* = 15.9, 8.6 Hz), 5.95(ddd, 1H, *J* = 15.7, 7.4, 1.2 Hz), 6.20(d, 1H, *J* = 15.9 Hz), 6.85(d, 4H, *J* = 7.3 Hz), 7.10(d, 4H, *J* = 7.3 Hz), 7.20(m, 10H). IR(neat) 3500, 2922, 2858, 1724, 1611, 1250 cm^{-1}. MS(m/e) 592(M^+), 471, 121(base peak). **3c**: TLC, SiO_2, EtOAc/hexanes 1 : 1, R_f = 0.36. ^1H NMR(300 MHz, $CDCl_3$) δ 0.95(d, 3H, *J* = 7.1 Hz), 2.35(bs, 1H), 2.65(m, 1H), 3.10(dd, 1H, *J* = 12.0, 6.0 Hz), 3.25(dd, 1H, *J* = 9.4, 8.1 Hz), 3.45(dd, 1H, *J* = 9.5, 3.4 Hz), 3.80(s, 6H), 4.0(d, 2H, *J* = 4.6 Hz), 4.25(m, 1H), 4.50(s, 4H), 5.15(dd, 1H, *J* = 10.2, 1.52 Hz), 5.40(m, 1H), 5.60(m, 2H), 6.90(d, 4H, *J* = 7.3 Hz), 7.25(d, 4H, *J* = 7.3 Hz). IR(neat) 3500, 2956, 2863, 1722, 1610, 1250 cm^{-1}. MS(m/e) 454(M^+), 333, 121(base peak). **3d**: TLC, SiO_2, EtOAc/hexanes 1 : 1, R_f = 0.37. ^1H NMR(200 MHz, $CDCl_3$) δ 2.40(m, 2H), 2.65(m, 1H), 3.35(m, 2H), 3.50(dd, 1H, *J* = 9.4, 3.4 Hz), 3.80(s, 6H), 4.10(d, 2H, *J* = 4.6 Hz), 4.40(m,1H), 4.50(s, 4H), 5.20(dd, 2H, *J* = 7.1, 4.0 Hz), 5.30(m, 1H), 5.60-5.80(m, 2H), 6.0(m, 1H), 6.60(dd, 1H, *J*= 14.9, 10.4 Hz), 6.90(d, 4H, *J* = 7.3 Hz), 7.25(d, 4H, *J* = 7.3 Hz). IR(neat) 3417, 2956, 2858, 1722, 1611, 1250 cm^{-1}. MS(m/e) 466(M^+), 438, 121(base peak).
4. The compound of **1c** was prepared from (2S, 3S)-2,3-*O*-isopropylidenedioxy-1,4-butanediol: (a) NaH, MPMCl, DMF, -30 °C, 2 h (80 %) (b) $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, -78 °C, 1 h (98%) (c) CBr_4, Ph_3P, CH_2Cl_2, 0 °C, 3 h, (70 %) (d)*n*BuLi, THF, -78 °C, 2 h (75 %) (e) *n*BuLi, EtBr, THF/ HMPA (3 : 1), -40 °C, 1 h (60 %) (f) H_2, $Pd/CaCO_3$ (quinoline), MeOH, rt, 12 h (90 %) (g) HCl(10 %), THF, rt, 12 h (80 %) (h) $CO(Im)_2$, CH_2Cl_2, rt, 30 min (85 %) and the compound **1d** was also prepared from(2S, 3S)-2,3-*O*-isopropylidenedioxy-1,4-butanetriol: (a)-(e): the same as the above sequence, (f) HCl(10 %), THF, rt, 12 h (80 %) (g) LAH, THF/ dioxane (1 : 7), reflux, 8 h (65 %) (h) $CO(Im)_2$, CH_2Cl_2, rt, 30 min (85 %). (2S, 3S)-2,3- *O*-isopropylidene dioxy-1,4-butanediol was prepared from diethyl L-tartrate by the procedure of Feit. See, Feit, P. W. *J. Med. Chem.* **1964**, *7*, 14.
5. The ratio of (*E*)- and (*Z*)- isomers for the methyl group at C(6) was determined by GC-MS analysis using VG-Instrument Trio 2000 GC-MS system (column: PONA, 25m, 0.2mm, 0.5 μm, oven temp.: 180 °C- 280 °C, carrier gas: He, injection temperature: 250 °C). The values of the retention time for (*E*)- isomer and (*Z*)- isomer were 5.19 min and 4.77 min, respectively.
6. The ratio of (5*S*)- and (5*R*)- at C(5) position was 3 : 2 and 3 : 1, respectively, which were deduced by the chemical shift for the methyl group in 300 MHz ^1H-NMR by comparison with the very similar compound in reference 1(d). The chemical shift for the (5*S*)- methyl group in **3c** showed a doublet at δ 0.95, whereas (5*R*)-methyl group showed at δ 0.96.The stereochemistry of C(6) position has not been determined.

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