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Neutral Alkylation of Chiral Allylic Cyclic Carbonates Catalyzed by Palladium Complex

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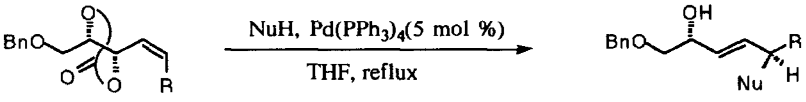
Abstract The cyclic carbonates of acyclic vinyl diols react with nucleophiles in the presence of a palladium complex as a catalyst under neutral conditions to afford alkylated *(E)*-allylic alcohols with highly regio-, and diastereoselectivity. This reaction represents an efficient 1,3-chirality transfer method.

Reaction of allylic compounds with various nucleophiles catalyzed by palladium complexes *via* π-allylpalladium complexes has been well established by Tsuji [1] and Trost.[2] In the literature, regioselective addition of nucleophiles to cyclic and acyclic vinyl epoxides or acyclic carbonates under neutral conditions *via* palladium(0) catalysis was reported,[3,4] and regio- and diastereoselective nucleophilic alkylation of sodiomalonate to chiral allylic lactone catalyzed by palladium(0) has been reported.[5] We have found that the cyclic carbonates **1**[6] underwent excellent regioselective alkylaton reactions under neutral conditions with nucleophiles in the presence of a palladium(0) catalyst in refluxing THF to form the *(E)*-allylic alcohols **2**.[7]



1 R = H, Me **2**

The results of the reactions of the cyclic carbonates **1a** and **1b** with nucleophiles are listed in Table 1. The carbonate **1a** reacted with diethyl malonate or ethyl acetoacetate in the presence of $Pd(PPh_3)_4$(5 mol %) in refluxing THF for 10 min or 20 min to give the *(E)*-allylic alcohols **2a**[8] and **2b**,[8] respectively, as the sole product (entries 1 and 2). The *(E)*-stereochemistry of the products **2a** and **2b** was determined by the ^{1}H-NMR (300 MHz) coupling constants of the two olefinic protons. The carbonate **1a** with phenyl allyl sulfone gave the isomerized product **2c**[8] (entry 3). For the substituted carbonate **1b**, diethyl malonate in the presence of a Pd catalyst, $Pd(PPh_3)_4$ (5 mol %), afforded **2d**[8] with remarkably high diastereoselectivity (entry 4). The diastereoselection of **2d** has been found to be nearly perfect (>99%) as judged by ^{1}H-NMR and GLC analysis of the acetate of **2d**.[9] Finally, phthalimide reacted with **1b** to afford **2e**[8] (entry 5). The typical procedure is as follows. To a stirred solution of the carbonate **1a** (470 mg, 2.00 mmol) in dry THF (10 ml) under N_2 was added diethyl malonate (482 mg, 2.40 mmol) and $Pd(PPh_3)_4$(5 mol %, 119 mg). After stirring for 10 min at reflux, the reaction mixture was cooled and THF was evaporated. The residue was separated by SiO_2 column chromatography (EtOAc/hexanes 1:2, R_f = 0.33) to afford **2a** (670 mg, 95%).

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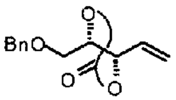
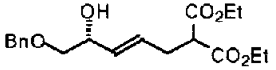
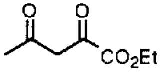
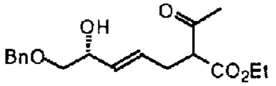
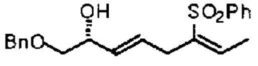
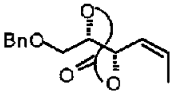
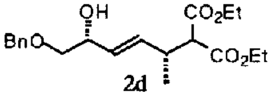
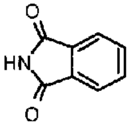
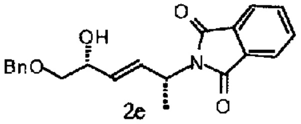
Table 1. Neutral alkylation of allylic cyclic carbonates with nucleophiles *via* palladium(0) catalysis.

Entry	Substrate	Nucleophile	Reaction Time	Product ^{a}	Isolated Yield(%)
1	 **1a**	$CH_2(CO_2Et)_2$	10 min	 **2a**	95
2	**1a**		20 min	 **2b**	85
3	**1a**		30 min	 **2c**	37
4	 **1b**	$CH_2(CO_2Et)_2$	10 min	 **2d**	93
5	**1b**		2 h	 **2e**	65

$^a[\alpha]_D^{25}$ values in $CHCl_3$. **2a**: -7.2 (*c* 1.5); **2b**: -5.68 (*c* 0.71); **2c**: -2.83 (*c* 0.32); **2d**: -7.62 (*c* 0.32); **2e**: -2.78 (*c* 0.65).

References and Notes

1. (a) Tsuji, J. *Acc. Chem. Res.* **1969**, *2*, 144. (b) Tsuji, J. *Organic Syntheses with Palladium Compounds*, Springer Verlag: West Berlin, 1980; pp 37-51. (c) Tsuji, J.; Minami, I. *Acc. Chem. Res.* **1987**, *20*, 140.
2. Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 358.
3. Tsuji, J.; Kataoka, H.; Kobayashi, Y. *Tetrahedron Lett.* **1981**, *22*, 2575.
4. Trost, B. M.; Molander, G. A. *J. Am. Chem. Soc.* **1981**, *103*, 5969.
5. Trost, B. M.; Klun, T. P. *J. Am. Chem. Soc.* **1981**, *103*, 1864.
6. Diastereoselective S_N2' addition of organocuprates to the cyclic carbonates **1** was also investigated; Kang, S-K.; Lee, D-H.; Sim, H-S.; Lim, J-S. *Tetrahedron Lett.* **1992**, in press.
7. The Pd catalyzed S_N2 reaction of the carbonate of 3-cyclohexene-1,2-diol with $NaCH(CO_2Me)_2$ was reported: Trost, B. M.; Runge, T. A. *J. Am. Chem. Soc.* **1981**, *103*, 7550.
8. The spectral data of all the compounds described are in agreement with assigned structures. Selected data are as follows. **2d**: ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.10 (d, 3 H, *J*= 6 Hz), 1.26 (t, 6 H, *J*= 7 Hz), 2.95 (m, 1 H), 3.25 (d, 1 H, *J*= 8 Hz), 3.32 (dd, 1 H, *J*= 14, 8 Hz), 3.48 (dd, 1 H, *J*= 10, 3 Hz), 4.17 (q, 4 H, *J*= 7 Hz), 4.30 (m, 1 H), 4.48 (s, 2 H), 5.54 (dd, 1 H, *J*= 16, 6 Hz), 5.76 (dd, 1 H, *J*= 16, 8 Hz), 7.34 (m, 5 H). MS(m/e) 346 (M-18). **2e**: ^{1}H-NMR ($CDCl_3$, 200 MHZ) δ 1.60 (d, 3 H, *J*= 8 Hz), 3.35 (dd, 1 H, *J*=10, 8 Hz), 3.56 (dd, 1 H, *J*= 8, 4 Hz), 4.35 (m, 1 H), 4.56 (s, 2 H), 4.95 (m, 1 H), 5.70 (dd, 1 H, *J* = 16 Hz, 5 Hz), 6.22 (dd, 1 H, *J*= 16, 8 Hz), 7.34 (m , 5 H), 7.70 (m, 2 H), 7.80 (m, 2 H). MS (m/e) 333 (M-18), 244.
9. Capillary GC analysis was performed for the acetate of **2d** using Hewlett Packard 5880 GC system (column: Hewlett-Packard SE-54, 0.2 mm x 16 m, oven temp: 150 → 300 °C, carrier gas: N_2, 1.0 ml/min, injection temp 280°C). The value of retention time was 8.2 min.