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PALLADIUM-CATALYZED COUPLING OF ALLYLIC CYCLIC CARBONATES WITH IODOBENZENE AND HYPERVALENT IODONIUM SALTS

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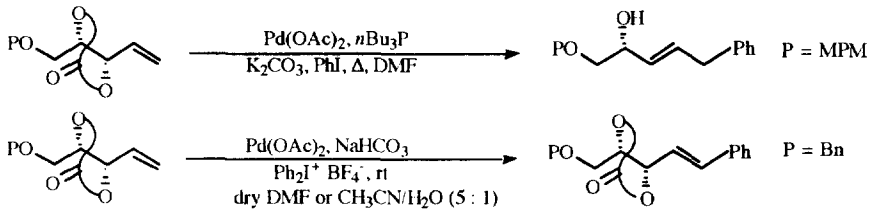
Abstract: Palladium-catalyzed arylation of allylic cyclic carbonates with iodobenzene in the presence of $Pd(OAc)_2$ as catalyst afforded the phenyl-substituted allylic alcohols *via* palladium oxygen β-elimination. However, palladium-catalyzed arylation, alkenylation, and alkynylation of allylic cyclic carbonates with iodonium tetrafluoroborates afforded the phenyl, alkenyl, and alkynyl-substituted allylic cyclic carbonates without reductive ring opening under aqueous and nonaqueous conditions.

Palladium-catalyzed reaction of organic halides with alkene(Heck-type reaction) is known to be a very convenient method for forming carbon-carbon bonds at unsubstituted vinylic position.[1] Recently, Larock [2] reported palladium-catalyzed arylation of vinylic epoxides and vinylic oxetanes with aryl halides to give aryl-substituted allylic and homoallylic alcohols *via* palladium oxygen β-elimination. Shimizu[3] reported the arylation of vinyl azetidinones without ring opening using palladium-catalyst in the presence of tetrabutylammonium chloride and potassium acetate as bases. In connection with our program to utilize cyclic carbonates in preparing chiral synthons utilizing Pd catalyst,[4] we have found that palladium catalyzes the arylation of allylic cyclic carbonates with iodobenzene to form allylic alcohols by reductive ring opening *via* palladium oxygen β-elimination. However, palladium-catalyzed arylation without reductive ring opening was accomplished with diphenyliodonium tetrafluoroborate, which are shown in Scheme 1.

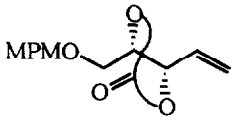
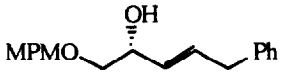
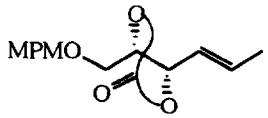
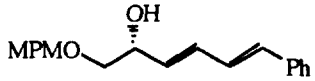
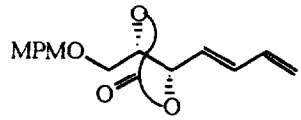
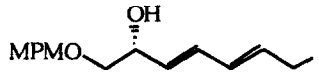
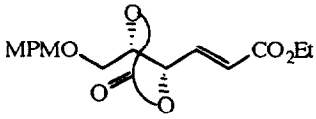
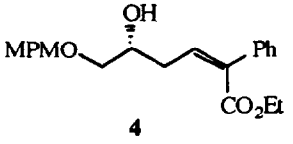
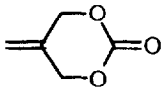
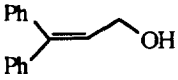


Scheme 1

The results of Pd-catalyzed arylation of allylic cyclic carbonates with iodobenzene are summarized in Table 1. The allylic cyclic carbonate **1a** was reacted with iodobenzene in the presence of $Pd(OAc)_2$(10 mol %), nBu_3P(20 mol %), and K_2CO_3(1.3 equiv) at 120 °C in DMF for 2 h to afford phenyl-substituted allylic alcohol **3a**[5](E : Z = 9 : 1) in 88% yield(entry 1). Alternatively, treatment of (E)-methyl-substituted allylic cyclic carbonate (E)-**1b** with iodobenzene in the presence of $Pd(OAc)_2$, nBu_3P, and K_2CO_3 in DMF provided 2,4-di-

enol **3b**[6] presumably *via* consecutive elimination and Heck-type arylation(entry 2).[2d] Treatment of **1c** with iodobenzene with the same catalysts using triethylamine and nBu_4NBr(TBAB) at 90 °C for 10 h afforded phenyl-substituted dienyl alcohol **3c** (*E*: *Z* = 10 : 1) in 90% yield(entry 3). It is notable that the unsaturated ester **1d** with iodobenzene in the presence of $Pd(OAc)_2$(10 mol %), nBu_3P(20 mol %), and Et_3N as base gave the isomerized product **4**[6](entry 4). Finally, for exomethylene cyclic carbonate **2**, reaction with 2 equiv of iodobenzene afforded diphenyl-substituted allylic alcohol **5**[5] in 93% yield(entry 5).[7]

Table 1. Palladium-Catalyzed Coupling of Allylic Cyclic Carbonates with Iodobenzene

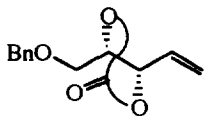
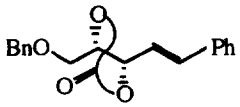
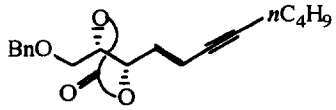
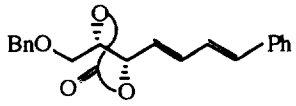
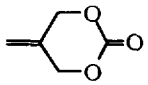
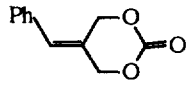
Entry	Substrate	Reaction Conditions[a]	Temp(°C)	Time(h)	Product[b,c]	Yield(%)[d]
1	 **1a**	$Pd(OAc)_2$(10 mol %) nBu_3P(20 mol %) K_2CO_3, PhI, DMF	120	2	 **3a** (*E*: *Z* = 9 : 1)	88
2	 (*E*)-**1b**	$Pd(OAc)_2$(10 mol %) nBu_3P(20 mol %) K_2CO_3, PhI, DMF	85	1	 **3b**	83
3	 **1c**	$Pd(OAc)_2$(10 mol %) nBu_3P(20 mol %) Et_3N, TBAB, PhI, DMF	90	10	 **3c** (*E*: *Z* = 10 : 1)	90
4	 **1d**	$Pd(OAc)_2$(10 mol %) nBu_3P(20 mol %) Et_3N, PhI, DMF	90	5	 **4**	80
5	 **2**	$Pd(OAc)_2$(10 mol %) nBu_3P(20 mol %) K_2CO_3, PhI, DMF	120	2	 **5**	93

[a] 1.3 equiv of base was used. [b] The ratio was determined by GC-MS using VG-Instrument Trio 2000 GC-MS system(column: PONA, 25 m, 0.3 mm, 0.5 μm, oven temp: 200 → 280 °C, carrier gas: He, injection temp: 250 °C). The retention times of **3a** were 11.6 min for (*E*)-isomer and 12.1 min for (*Z*)-isomer. **3c**: The retention times were 18.9 min for (*E*)-isomer and 18.3 min for (*Z*)-isomer. [c] The values of $[\alpha]_D^{25}$ in $CDCl_3$. **3a**: -12.9(*c* 0.2); **3b**: +10(*c* 0.1); **3c**: -11.0(*c* 0.2); **4**: -12.5(*c* 0.3). [d] The yields are isolated yields.

Alternatively, we have investigated palladium-catalyzed coupling with hypervalent iodonium compounds [8,9] in order to achieve the coupling under mild conditions without ring opening which is summarized in Table 2. Thus, when the allylic cyclic carbonate **1e** was treated[10] with 1 equiv of diphenyoliodonium tetrafluoroborate at room temperature in dry DMF or CH_3CN/H_2O (5 : 1), the normal Heck-type reaction product **6a**[5] without ring opening was obtained in 97% and 97% yields,

respectively(Method A and B in entry 1). This coupling was also carried out for alkenyl(phenyl)iodonium salts. It is noteworthy that the reaction of **1e** with 1-hexynyl(phenyl)iodonium tetrafluoroborate under nonaqueous and aqueous conditions afforded the coupled product **6b**[5] without any side products (Method A and B in entry 2). Using (*E*)-2-phenylethenyl(phenyl)iodonium tetrafluoroborate, the phenyl-substituted (*E,E*)-dienyl cyclic carbonate **6c**[5] was obtained in 97% and 96% yields, respectively(entry 3). Finally, exomethylene cyclic carbonate **2** was phenylated with diphenyliodonium tetrafluoroborate in dry DMF to afford **7**[5] without any ring opening(entry 4).[11, 12] Presumably, iodonium salts might be better electrophiles which facilitate the oxidative addition with the catalytic Pd(0) species and allow the coupling under mild conditions.

Table 2. Pd-Catalyzed Coupling of Allylic Cyclic Carbonates with Iodonium Tetrafluoroborates under Nonaqueous and Aqueous Conditions

Entry	Substrates	Iodonium Salts[a]	Reaction conditions[b]	Product[c]	Yield(%)
1	 **1e**	$Ph_2I^+ BF_4^-$	A	 **6a**	97
			B		97
2	**1e**	$nC_4H_9C{\equiv}C{-}I^+(Ph)\ BF_4^-$	A	 **6b**	92
			B		94
3	**1e**	(*E*)-$PhCH{=}CH{-}I^+(Ph)\ BF_4^-$	A	 **6c**	97
			B		96
4	 **2**	$Ph_2I^+ BF_4^-$	A	 **7**	85

[a] The iodonium salts were prepared by Ochiai's procedure. See ref. 9. [b] All the reactions were run with the carbonate (1 equiv) and iodonium salt (1 equiv) in the presence of $Pd(OAc)_2$ (5 mol %) and $NaHCO_3$ (2 equiv) at room temperature. Method A: dry DMF, 2 h(nonaqueous conditions); Method B: CH_3CN/H_2O (5 :1), 1.5 h(aqueous conditions). [c] The values of $[\alpha]_D^{25}$ in $CHCl_3$. **6a**: -116(*c* 0.8); **6b**: -18(*c* 0.12); **6c**: -92(*c* 1.4).

In summary, palladium-catalyzed arylation of allylic cyclic carbonates with or without ring opening can be controlled by an appropriate choice of iodobenzene or diphenyliodonium tetrafluoroborate.

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

References and Notes

1. (a) Heck, R. F. *Org. React.* **1982**, *27*, 345. (b) Heck, R. F. *Acc. Chem. Res.* **1979**, *12*, 146. (c) Heck, R. F. *In Palladium Reagents in Organic Syntheses*; Academic Press: London, **1985**.
2. (a) Larock, R. C.; Leung, W-Y. *J. Org. Chem.* **1990**, *55*, 6244. (b) Larock, R. C.; Ilkka, S. J. *Tetrahedron*

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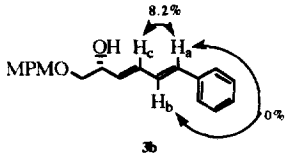
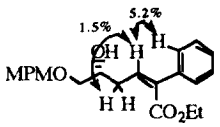
3. Satake, A; Okano, K.; Shimizu, I.; Yamamoto, A. *Synlett* **1994**, 839.
4. (a) Kang, S-K.; Kim, S-G.; Lee, J-S. *Tetrahedron: Asymmetry* **1992**, *3*, 1139. (b) Kang, S-K.; Park, D-C.; Jeon, J-H.; Rho, H-S.; Yu, C-M. *Tetrahedron Lett.* **1994**, *35*, 2357. (c) Kang, S-K.; Park, D-C.; Cho, D-G.; Chung, J-U.; Jung, K-Y. *J. Chem. Soc. Perkin Trans. 1*. **1994**, 237. (d) Kang, S-K.; Park, D-C.; Park, C-H.; Hong, R-K. *Tetrahedron Lett.* **1995**, *36*, 405.
5. Satisfactory spectral and physical data were obtained for the new compounds in accord with the structure. Selected physical and spectral data are as follows. **3a**: ^{1}H NMR(200 MHz, $CDCl_3$) δ 1.75(bs, 1H), 3.30-3.55(m, 4H), 3.80(s, 3H), 4.30(m, 1H), 4.50(s, 2H), 5.50(dd, 1H, *J* = 15.3, 6.3 Hz), 5.93(dd, 1H, *J* = 15.6, 6.7 Hz), 6.90(d, 2H, *J* = 8.7 Hz), 7.25(m, 7H). IR (neat) 3400, 2925, 2855, 1611, 1246 cm^{-1}. MS(m/e) 298(M$^+$), 136, 121(base peak), 117, 91, 77. **3b**: ^{1}H NMR(200 MHz, $CDCl_3$) δ 2.50(bs, 1H), 3.38(dd, 1H, *J* = 9.6, 8.0 Hz), 3.53 (dd, 1H, *J* = 9.6, 3.4 Hz), 3.80(s, 3H), 4.50(s, 2H), 4.62(m, 1H), 5.74 (dd, 1H, *J* = 15.0, 6.3 Hz), 6.50(m, 2H), 6.75(d, 1H, *J* = 11.0 Hz), 6.90(d, 2H, *J* = 8.7 Hz), 7.30(m, 7H). IR(neat) 3375, 2950, 2850, 1612, 1247 cm^{-1}. MS(m/e) 310(M$^+$), 159, 128, 121(base peak), 77. **3c**: ^{1}H NMR(300 MHz, $CDCl_3$) δ 2.40(bs, 1H), 3.30-3.60(m, 4H), 3.80(s, 3H), 4.35(m, 1H), 4.50(s, 2H), 5.45-5.90(m, 2H), 6.10(m, 1H), 6.90(d, 2H, *J* = 8.7 Hz), 7.25(m, 7H). IR (neat) 3410, 2924, 2858, 1724, 1611, 1249 cm^{-1}. MS(m/e) 324(M$^+$), 202, 121(base peak), 91, 77. **4**: ^{1}H NMR(300 MHz, $CDCl_3$) δ 1.41(t, 3H, *J* = 7.15 Hz), 2.55(bs, 1H), 3.80(m, 5H), 4.40(q, 2H, *J* = 7.15 Hz), 4.50-4.70(m, 5H), 6.90(m, 3H), 7.30(m, 7H). IR (neat) 3500, 2920, 2850, 1714, 1248 cm^{-1}. MS(m/e) 370(M$^+$), 297, 292, 137, 121(base peak), 77. **5**: ^{1}H NMR(300 MHz, $CDCl_3$) δ 3.15(bs, 1H), 4.10(d, 2H, *J* = 5.9 Hz), 7.40(m, 11H). IR(neat) 3412, 2923, 2853 cm^{-1}. MS(m/e) 210(M$^+$), 133, 77, 57. **6a**: ^{1}H NMR(300 MHz, $CDCl_3$) δ 3.67(dd, 1H, *J* = 12.0, 4.0 Hz), 3.80(dd, 1H, *J* = 12.0, 4.0 Hz), 4.53 (m, 1H), 4.64(d, 2H, *J* = 6.4 Hz), 5.17(dd, 1H, *J* = 7.3, 7.3 Hz), 6.17 (dd, 1H, *J* = 15.8, 7.8 Hz), 6.71(d, 1H, *J* = 15.8 Hz), 7.36(m, 10H). IR(neat) 3050, 3025, 1805 cm^{-1}. MS(m/e) 219(M$^+$), 131, 115, 91(base peak). **6b**: ^{1}H NMR(400 MHz, $CDCl_3$) δ 0.87(t, 3H, *J* = 5.1 Hz), 1.56(m, 4H), 2.18(t, 2H, *J* = 6.1 Hz), 3.68(dd, 1H, *J* = 11.4, 3.7 Hz), 3.80(dd, 1H, *J* = 11.4, 3.7 Hz), 4.19(m, 1H), 4.63(d, 2H, *J* = 6.0 Hz), 5.19(dd, 1H, *J* = 7.5, 7.5 Hz), 6.17(dd, 1H, *J* = 16.2, 7.8 Hz), 6.71(d, 1H, *J* = 16.2 Hz), 7.27(m, 5H). IR(neat) 3061, 2956, 1804 cm^{-1}. MS(m/e) 208(M$^+$), 118, 115, 117(base peak), 91. **6c**: ^{1}H NMR(400 MHz, $CDCl_3$) δ 3.54(dd, 1H, *J* = 11.2, 3.7 Hz), 3.66(dd, 1H, *J* = 7.2, 7.2 Hz), 4.34(m, 1H), 4.52(d, 2H, *J* = 6.8Hz), 5.12(dd, 1H, *J* = 7.2, 7.2Hz), 6.12(dd,1H, *J* = 16.0, 7.9 Hz), 6.65(d, 1H, *J* = 16.0 Hz), 7.08(m, 2H), 7.26(m, 10 H). IR(neat) 3062, 3031, 1806 cm^{-1}. MS(m/e) 172, 128, 107, 91(base peak), 79. **7**: ^{1}H NMR(300 MHz, $CDCl_3$) δ 4.83(s, 2H), 4.95(s, 2H), 6.74(s, 1H), 7.37(m, 5H). IR(neat) 3059, 3027, 1741 cm^{-1}. MS(m/e) 191(M$^+$), 190, 145, 117, 115(base peak), 78.
6. The stereochemistry in **3b** and **4** was determined by noe experiment using 300 MHz ^{1}H NMR.



3b



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7. The typical procedure is as follows. Preparation of **3b**: To a stirred solution of $Pd(OAc)_2$(16 mg, 10 mol %), nBu$_3$P(32 mg, 20 mol %), and K_2CO_3(127 mg, 0.92 mmol) in dry DMF(1 mL) was added (*E*)-**1b**(200 mg, 0.70 mmol) in dry DMF(1 mL) followed by iodobenzene(180 mg, 0.92 mmol). The reaction mixture was stirred at 85°C for 1 h and then cooled and extracted with ether. The organic layer was dried over anhydrous $MgSO_4$ and evaporated *in vacuo*. The crude product was separated by SiO_2 column chromatography (EtOAc/hexanes 1 : 2, R_f = 0.53) to afford **3b**(226 mg, 83%).
8. Palladium-catalyzed coupling of alkenyl(phenyl)iodonium salts and olefins was reported by Moriarty. See: Moriarty, R. M.; Epa, W. R.; Awasthi, A. K. *J. Am. Chem. Soc.* **1991**, *113*, 6315.
9. Ochiai, M.; Sumi, K.; Takaoka, Y.; Nagao, Y.; Shiro, M.; Fujita, E. *Tetrahedron* **1988**, *44*, 4095.
10. In the coupling of alkenyl(phenyl)iodonium salts with olefins, 3 equiv of olefins were used. See, reference 8. In the palladium-catalyzed cross-coupling of alkenyl(phenyl)iodonium salts with organotin compounds, for the iodonium salts excess organotin compounds were used. See, Moriarty, R. M.; Epa, W. R. *Tetrahedron Lett.* **1992**, *33*, 4095.
11. The typical procedure is as follows. Preparation of **6a**(Method A): To a mixture of diphenyliodonium tetrafluoroborate(172 mg, 0.46 mmol) and $Pd(OAc)_2$(4 mg, 5 mol %) was added $NaHCO_3$(77 mg, 0.92 mmol) followed by allylic cyclic carbonate **1e**(110 mg, 0.46 mmol) in DMF(5 mL) under nitrogen atomosphere at room temperature. The reaction mixture was stirred at room temperature for 2 h and quenched with saturated NH_4Cl solution and then extracted with ether(20 mL x 2). The organic layer was dried over $MgSO_4$ and evaporated *in vacuo*. The crude product was separated by SiO_2 column chromatography (EtOAc/hexanes 1 : 4, R_f = 0.70) to give **6a** (140 mg, 97%). In method B, for the same quantities of substrates, the same conditions were applied except CH_3CN/H_2O (5 : 1) (5 mL) as solvent and stirring for 1.5 h.
12. The amounts of $Pd(OAc)_2$ catalyst and base can be reduced 2 mol % and 1 equiv, respectively. Water only can be used as solvent, but the yields were lower. The reactions proceeded in the absence of base, which resulted in the formation of some side products.

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