Pergamon

Tetrahedron Letters 39 (1998) 2127–2130

TETRAHEDRON
LETTERS

Palladium-Catalyzed Arylation of α-Allenic Alcohols with Hypervalent Iodonium Salts: Synthesis of Epoxides and Diol Cyclic Carbonates

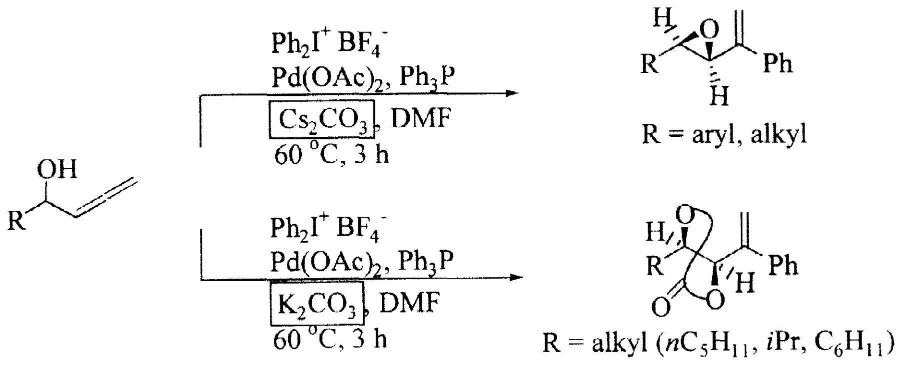
Suk-Ku Kang,* Tokutaro Yamaguchi, Sung-Jae Pyun, Yong-Tack Lee,
and Tae-Gon Baik

Department of Chemistry, Sung Kyun Kwan University,
Natural Science Campus, Suwon 440-746, Korea

Received 5 January 1998; accepted 6 January 1998

Abstract: *Pd(0)-catalyzed arylation of the aryl-substituted α-allenic alcohols with hypervalent iodonium salts afforded substituted trans-epoxides. Alternatively, arylation of the alkyl-substituted α-allenic alcohols in the presence of K_2CO_3 afforded syn-diol cyclic carbonates and trans-epoxides in the presence of Cs_2CO_3.*

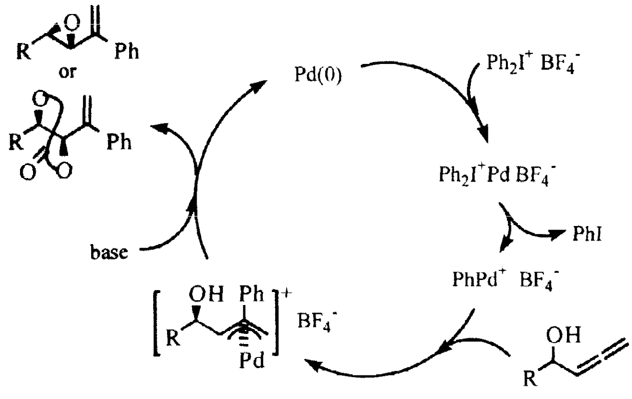
Palladium-catalyzed arylation or alkenylation of allenes to form π-allylpalladium complexes, which undergo substitution by nucleophiles, is known.[1,2] However, in the absence of nucleophiles, 1,3-dienes are formed by β-elimination of PdH from π-allyl palladium complexes. Thus in the case of α-allenic alcohols, palladium-catalyzed arylation or alkenylation with aryl or alkenyl halides afforded β-methyl-α,β-unsaturated carbonyl compounds.[3] In connection with our programs to utilize iodonium salts[4] in palladium-catalyzed coupling,[5] we have investigated the coupling of iodonium salts with α-allenic alcohols and found that hydroxyl group adjacent to allenic moiety acts as a nucleophile to π-allylpalladium complexes and palladium-catalyzed arylation of aryl-substituted α-allenic alcohols afforded *trans*-epoxides. However, treatment of alkyl-substituted α-allenic alcohols under the same conditions in the presence of K_2CO_3 as base resulted in the formation of *syn*-diol cyclic carbonates and *trans*-epoxides with Cs_2CO_3 as base (Scheme 1).[6]



Scheme 1

PII: S0040-4039(98)00076-8

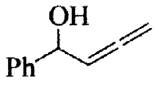
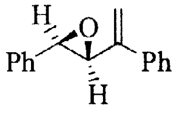
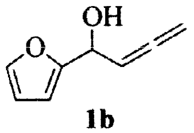
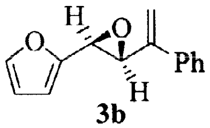
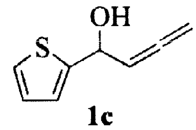
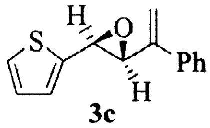
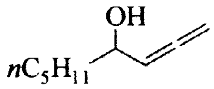
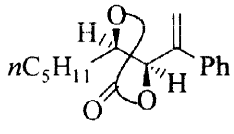
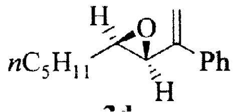
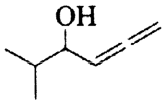
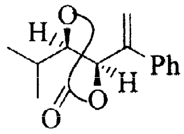
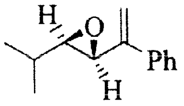
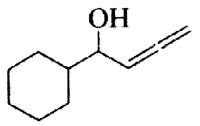
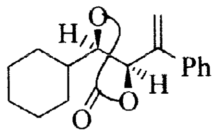
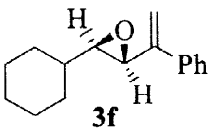
The palladium-catalyzed phenylation of α-allenic alcohols[7] with diphenyliodonium tetrafluoroborate (**2a**) is summarized in Table 1.[8] The phenyl-substituted α-allenic alcohol **1a** was reacted with diphenyliodonium tetrafluoroborate (2a) in the presence of $Pd(OAc)_2$ (5 mol %) and Ph_3P (0.2 equiv) as catalysts and K_2CO_3 or Cs_2CO_3 as base in DMF at 60 °C for 3 h to afford phenyl-substituted vinyl *trans*-epoxide **3a**[8] as the sole product in 62% or 60% yields, respectively (entry 1).[9] The *trans*-epoxide was confirmed by the analysis of 300 MHz ^1H NMR spectrum. Of the ligand other than Ph_3P tested, dppe, dppp, and tri-*o*-tolylphosphine were not effective.[10] Under the same conditions, 2-furyl- and 2-thienyl-substituted α-allenic alcohols **1b** and **1c** afforded *trans*-epoxides **3b** and **3c** (entries 2 and 3). Surprisingly enough, in the case of alkyl-substituted allenic alcohols, we have found that the base is crucial in the formation of the product. Treatment of the alkyl-substituted α-allenic alcohols **1d** and $Ph_2I^+ BF_4^-$ (**2a**) with catalytic amounts of $Pd(OAc)_2$ and Ph_3P in the presence of K_2CO_3 as base, *syn*-diol cyclic carbonate **4a**[8] was obtained in 76% yield without formation of epoxides (entry 4). However under the same conditions using the more basic Cs_2CO_3 *trans*-epoxide **3d** was afforded (entry 5). For the formation of epoxides or carbonates the plausible mechanism is shown in Scheme 2. Presumably, when less basic K_2CO_3 was used, palladium-catalyzed arylation of allenic moiety would give π-allylpalladium complex, which in turn converted to carboxylate anion formed from K_2CO_3 and hydroxyl group followed by attack to π-allylpalladium complex stereoselectively in an internal substitution. For the isopropyl- and cyclohexyl-substituted allenic alcohols **1e** and **1f**, conducting the reactions in the presence of K_2CO_3 provided cyclic carbonates **4b** and **4c** (entries 6 and 8), whereas in the presence of Cs_2CO_3 **1e** and **1f** gave *trans*-epoxides **3e** and **3f** (entries 7 and 9).



Scheme 2

Alternatively, we have examined the reaction of the other iodonium salts **2b** and **2c** with α-allenic alcohols, which resulted in the formation of separable mixtures of *trans*-epoxides and cyclic carbonates, shown in Scheme 3. When the α-allenic alcohol **1a** was reacted with diaryl iodonium salt **2b**, *trans*-epoxides **3g** and **3a** were formed in the ratio of 58 : 27, which were readily separable by SiO_2 column chromatography. Similarly, arylation of **1a** with 2-thienylphenyliodonium tetrafluoroborate (**2c**) gave **3h** and **3a** in the ratio of 1 : 2. Finally, the alkyl-substituted α-allenic alcohol **1d** was arylated with iodonium salts **2b** and **2c** to afford separable mixtures of **4a**, **4d**, and **4e**.

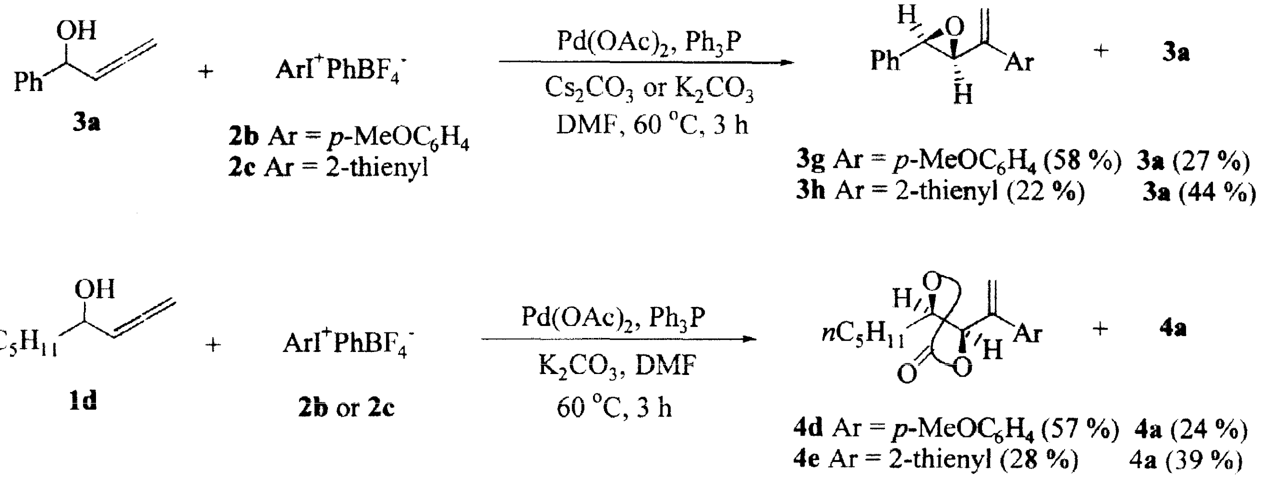
Table 1. Pd-Catalyzed Phenylation of α-Allenic Alcohols (**1**) with Diphenyliodonium Tetrafluoroborate (**2a**)

Entry	Substrate	Base	Product	Yield (%)[a]
1	 **1a**	K_2CO_3 (Cs_2CO_3)	 **3a**	62 (60)[b]
2	 **1b**	K_2CO_3 (Cs_2CO_3)	 **3b**	52 (63)[b]
3	 **1c**	K_2CO_3 (Cs_2CO_3)	 **3c**	48 (51)[b]
4	 **1d**	K_2CO_3	 **4a**	76
5	**1d**	Cs_2CO_3	 **3d**	65
6	 **1e**	K_2CO_3	 **4b**	73
7	**1e**	Cs_2CO_3	 **3e**	59
8	 **1f**	K_2CO_3	 **4c**	68
9	**1f**	Cs_2CO_3	 **3f**	62

---

[a] Isolated yields. [b] The yields in parenthesis are the isolated yields conducted in the presence of Cs_2CO_3

In summary, palladium-catalyzed arylation of aryl-substituted α-allenic alcohols with hypervalent iodonium salts in the presence of K_2CO_3 or Cs_2CO_3 afforded *trans*-epoxides. Alternatively, arylation of alkyl-substituted α-allenic alcohols afforded *syn*-diol cyclic carbonates in the presence of K_2CO_3 as base.[11]



Scheme 3

References and Notes

1. (a) Djahanbuni, D.; Cazes, B.; Gore, J. *Tetrahedron Lett.* **1984**, *25*, 203-206. (b) Nokami, J.; Maihara, A.; Tsuji, J. *Tetrahedron Lett.* **1990**, *31*, 5629-5630. (c) Larock, R. C.; Berrios-Pena, N.G.; Fried, C. A. *J. Org. Chem.* **1991**, *56*, 2615-2617. (d) Yamamoto, Y.; Al-Masum, M.; Asao, N. *J. Am. Chem. Soc.* **1994**, *116*, 6019-6020.
2. Cazes, B. *Pure Appl. Chem.* **1990**, *62*, 1867-1878.
3. Shimizu, I.; Sugiura, T.; Tsuji, J. *J. Org. Chem.* **1985**, *50*, 537-539.
4. For recent reviews: (a) Stang, P. J. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 274-285. (b) Moriarty, R. M.; Viad, R. K. *Synthesis* **1990**, 431-447. (c) Ochiai, M. *Rev. Heteroatm. Chem.* 1989, *2*, 92-111.
5. (a) Kang, S-K.; Lee, H-W.; Kim, J-S.; Choi, S-C. *Tetrahedron Lett.* **1996**, *37*, 3723-3726. (b) Kang, S-K.; Lee, H-W.; Jang, S-B.; Ho, P-S. *J. Org. Chem.* **1996**, *61*, 4720-4724. (c) Kang, S-K.; Lee, H-W.; Jang, S-B.; Ho, P-S. *J. Chem. Soc. Chem. Commun.* **1996**, 835-836. (d) Kang, S-K.; Jung, K-Y.; Park, C-H.; Jang, S-B. *Tetrahedron Lett.* **1995**, *36*, 8047-8050. (e) Kang, S-K.; Lee, H-W.; Jang, S-B.; Kim, T-H.; Pyun, S-J. *J. Org. Chem.* **1996**, *61*, 2604-2605.
6. The α-allenic alcohols were converted to *syn*-diol *via* iodocyclization: Friesen, R.W.; Giroux, A. *Tetrahedron Lett.* **1993**, *34*, 1867-1870.
7. Crabbe, P.; Nassim, B.; Rovert-Lopes, M. T. *Org. Synth.* **1984**, *63*, 203-205.
8. Satisfactory spectral data were obtained in accordance with the structure. Selected NMR data are as follows. **3a**: ^1H NMR ($CDCl_3$, 300 MHz) δ 3.69 (dd, 1H, J = 1.8 Hz, 0.9 Hz), 3.72 (d, 1H, J = 1.8 Hz), 5.49 (dd, 1H, J = 1.2 Hz, 0.9 Hz), 5.52 (d, 1H, J = 1.2 Hz), 7.2-7.4 (m, 10H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 61.53, 62.50, 112.06, 125.60, 126.05, 128.13, 128.39, 128.53, 128.62, 136.99, 137.71, 143.93. **4a**: ^1H NMR ($CDCl_3$, 400 MHz) δ 0.86-1.70 (m, 11H), 4.28 (m, 1H), 5.10 (d, 1H, J = 6.2 Hz), 5.47 (s, 1H), 5.51 (d, 1H, J = 0.8 Hz), 7.3-7.4 (m, 5H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.81, 22.27, 24.05, 31.09, 33.92, 81.55, 82.41, 116.70, 127.20, 128.70, 128.87, 136.90, 143.84, 154.37.
9. The typical procedure for the preparation of *trans*-epoxide **3a** is as follows. To a stirred solution of $Ph_2I^+BF_4^-$ (**2a**) (302 mg, 0.82 mmol) and K_2CO_3 (237 mg, 1.71 mmol) and Ph_3P (36 mg, 0.14 mmol) in DMF was added $Pd(OAc)_2$ (8 mg, 5 mol %) followed by α-allenic alcohol **1a** (100 mg, 0.68 mmol) in DMF (1 mL). The reaction mixture was stirred at 60 °C for 3 h and cooled to room temperature and quenched with saturated NH_4Cl solution. The mixture was extracted with ether and 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 : 10, R_f = 0.55) to afford the *trans*-epoxide **3a** (93.7 mg, 62%).
10. As base, K_2CO_3 and Cs_2CO_3 were suitable and $NaHCO_3$ and pyrrolidine did not give the product. The base Et_3N gave phenyl-substituted ketone *via* β-elimination of the proton adjacent to hydroxy group along with *trans*-epoxide **3a** in the ratio of 2 : 1. As solvent DMSO can be used but THF was not effective. With NMP and CH_3CN, the major product was ketone instead of *trans*-epoxide.
11. Generous financial support from KOSEF (97-0501-02-01-3) and Ministry of Education (BSRI-97-3420) is gratefully acknowledged.