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

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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 . © 1998 Elsevier Science Ltd. All rights reserved.

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 salts⁴ 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 palladiumcatalyzed 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 K₂CO₃ as base resulted in the formation of *syn*-diol cyclic carbonates and *trans*-epoxides with Cs₂CO₃ as base (Scheme 1).⁶



Scheme 1

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The palladium-catalyzed phenylation of α -allenic alcohols⁷ 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 Ph₃P (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 transepoxide **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 MHz⁴H NMR spectrum. Of the ligand other than Ph₃P 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 Ph₂I⁺ BF₄⁻ (2a) with catalytic amounts of Pd(OAc)₂ and Ph₃P 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 Cs₂CO₃ 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 K2CO3 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 Cs₂CO₃ 1e and 1f gave *trans*-epoxides 3e and 3f (entries 7 and 9).





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 SiO₂ 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**.

| Entry | Substrate | Base | Product | Yield (%) ^a |
|-------|---------------------------------|---|--|------------------------|
| 1 | OH Ph | K ₂ CO ₃ (Cs ₂ CO ₃) | Ph Ph Ph | 62 (60) ^b |
| 2 | O Ib | K_2CO_3 (Cs_2CO_3) | O H O H Ph 3b | 52 (63) ^b |
| 3 | S Ic | K ₂ CO ₃ (Cs ₂ CO ₃) | S B B B B C B B B B B B B B B B B B B B | 48 (51) ^b |
| 4 | nC ₅ H ₁₁ | K ₂ CO ₃ | $nC_{5}H_{11}$ H_{11} H_{1 | 76 |
| 5 | 1d | Cs ₂ CO ₃ | $nC_{3}H_{11}$ Ph 3d | 65 |
| 6 | OH le | K ₂ CO ₃ | $H_{/I}^{O}$ $H_{/H}^{O}$ Ph | 73 |
| 7 | 1e | Cs ₂ CO ₃ | H O Ph | 59 |
| 8 | OH If | K ₂ CO ₃ | $ \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \end{array}\\ \end{array}\\ \end{array}\\ \end{array}\\ \begin{array}{c} \end{array}\\ \end{array} $ | 68 |
| 9 | lf | Cs ₂ CO ₃ | H O Ph 3f | 62 |

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

^a Isolated yields. ^b The yields in parenthesis are the isolated yields conducted in the presence of Cs₂CO₃

In summary, palladium-catalyzed arylation of aryl-substituted α -allenic alcohols with hypervalent iodonium salts in the presence of K₂CO₃ or Cs₂CO₃ afforded *trans*-epoxides. Alternatively, arylation of alkyl-substituted α -allenic alcohols afforded *syn*-diol cyclic carbonates in the presence of K₂CO₃ as base.¹¹



4d Ar = p-MeOC₆H₄ (57 %) **4a** (24 %) **4e** Ar = 2-thienyl (28 %) **4a** (39 %)

Scheme 3

References and Notes

- (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.
- 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.
- (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.
- 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.
- Satisfactory spectral data were obtained in accordance with the structure. Selected NMR data are as follows. 3a: ¹H NMR (CDCl₃, 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). ¹³C NMR (CDCl₃, 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 (CDCl₃, 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). ¹⁴C NMR (CDCl₃, 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 Ph₂I⁺BF₄ (**2a**) (302 mg, 0.82 mmol) and K₂CO₃ (237 mg, 1.71 mmol) and Ph₁P (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 NH₄Cl solution. The mixture was extracted with ether and the organic layer was dried over anhydrous MgSO₄ and evaporated *in vacuo*. The crude product was separated by SiO₂ column chromatography (EtOAc/hexanes = 1 : 10, R_t = 0.55) to afford the *trans*-epoxide **3a** (93.7 mg, 62%).
- 10. As base, K-CO₃ and Cs-CO₃ were suitable and NaHCO₃ and pyrrolidine did not give the product. The base Et₃N 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 CH₃CN, the major product was ketone instead of *trans*-epoxide.
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