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Palladium(II) Acetate Catalyzed Tandem Cycloisomerization and Oxidation of Arylvinylcyclopropenes Using *p*-Benzoquinone as Oxidant and Pro-nucleophile

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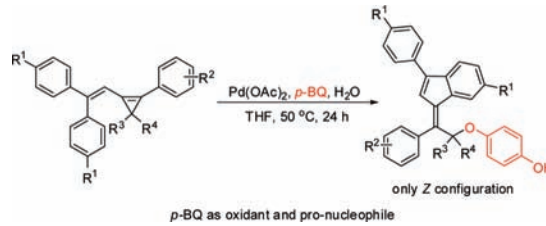
ABSTRACT



Catalyzed by Pd(II)/*p*-BQ, a tandem cycloisomerization and oxidation of arylvinylcyclopropenes took place smoothly to produce methyleneindene derivatives stereoselectively in moderate to excellent yields, affording an unusual example of solo addition by *p*-hydroquinone generated by oxidation of Pd(0) to Pd(II) along with the formation of a new C−O bond.

p-BQ (*p*-benzoquinone) has been widely used in organic synthesis as a dienophile in Diels−Alder reactions[1] or as an oxidation or dehydrogenation agent in many organic reactions.[2] Additionally, the reaction of *p*-BQ with enamines has been widely used to prepare 5-hydroxyindole derivatives[3] and cycloparaphenylenes under mild conditions.[4] Among these useful applications, *p*-BQ acting as an oxidant in Pd-catalyzed reactions has also been extensively studied in recent decades.[5,6] For example, Bäckvall and co-workers have done a pioneering work and mechanistic study on the Pd(II)/Pd(0)−benzoquinone/hydroquinone redox system.[7] Compared with ordinary olefins and cyclopentenes/cyclohexenes, studies on the palladium-catalyzed oxidation of highly strained small rings are rare.[8] Cyclopropenes,[9] as the smallest cycloolefins, are highly strained but readily accessible substances,[10] which have been serving as useful building

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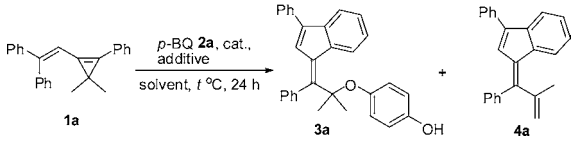
blocks in many organic reactions.[11] On the basis of the studies of acid/transition-metal-catalyzed reactions of several highly strained small ring substances,[12] we attempted to examine the Pd-catalyzed oxidation of arylvinylcyclopropenes **1** in the presence of *p*-BQ. In this paper, we wish to report the Pd-catalyzed tandem cycloisomerization and oxidation reactions of arylvinylcyclopropenes with *p*-BQ as oxidant and pro-nucleophile.

Initial examination of the reaction was performed by using (2-(3,3-dimethyl-2-phenylcycloprop-1-enyl)ethene-1,1-diyl)dibenzene (**1a**, 0.1 mmol) and *p*-BQ (**2a**, 0.2 mmol) as the substrates in the presence of Pd catalyst and acetic acid (HOAc) (0.2 mmol) to develop the optimized reaction conditions, and the results of these experiments are summarized in Table 1. We found that (*Z*)-4-(2-methyl-1-phenyl-

Table 1. Pd-Catalyzed Tandem Cycloisomerization and Oxidation of Cyclopropenes in the Presence of Various Pd Sources and Additives

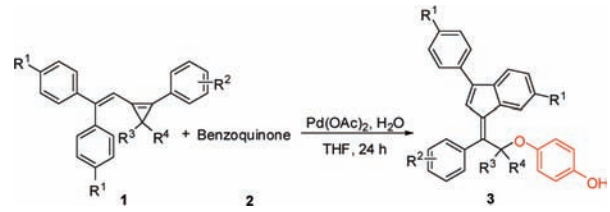


entry[a]	cat.	mol %	additive	solvent	temp (°C)	yield[b] (%) 3a	4a
1	$Pd(OAc)_2$	10	HOAc	DCE	50	93	trace
2[c]	$Pd(OAc)_2$	10	HOAc	DCE	50	60	33
3	$Pd(OAc)_2$	1.0 equiv	HOAc	DCE	50	44	trace
4	$Pd(OAc)_2$	1.0 equiv	–	DCE	50	49	trace
5	$Pd(OAc)_2$	5	air	DCE	50	5	–
6	$Pd(OAc)_2$	5	H_2O	DCE	50	93	trace
7	$Pd(OAc)_2$	5	H_2O	DCM	rt	–	–
8	$Pd(OAc)_2$	5	H_2O	THF	50	97	–
9	$Pd(OAc)_2$	5	–	acetone/H_2O	50	–	–
10	$Pd(OAc)_2$	5	H_2O	CH_3CN	50	16	–
11	$Pd(OAc)_2$	5	H_2O	toluene	50	23	trace
12	$PdCl_2$	10	H_2O	THF	50	complex	
13	$Pd(PPh_3)_4$[d]	5	H_2O	THF	50	<5	–
14	$Pd(PPh_3)_4$[d]	1.0 equiv	H_2O	THF	50	52	–
15	$Pd(OAc)_2$	5	H_2O[e]	THF	50	90	–
16	–	–	H_2O	THF	50	–	–

[a] Unless otherwise specified, all reactions were carried out using **1a** (0.1 mmol), *p*-BQ (**2a**, 0.2 mmol), additives (0.2 mmol) in the presence of listed catalyst for 24 h. [b] Isolated yields. [c] Reaction was carried out for 72 h. [d] 0.2 mmol of *p*-hydroquinone instead of *p*-BQ . [e] 2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO, 0.2 mmol) was added.

1-(3-phenyl-1*H*-inden-1-ylidene)propan-2-yloxy)phenol **3a** was produced as the major product in 93% yield along with trace of (*E*)-1-(2-methyl-1-phenylallylidene)-3-phenyl-1*H*-indene **4a** in 1,2-dichloroethane (DCE) at 50 °C after 24 h without the formation of any O-acetylation product (Table 1, entry 1). The structure of **3a** was unambiguously determined by X-ray diffraction of its analogue **3c** (Table 2, entry 2). Its ORTEP drawing is shown in Figure 1, and its CIF data are presented in the Supporting Information.[13] Extending reaction time to 72 h produced **3a** in 60% yield and **4a** in 33% yield (Table 1, entry 2), suggesting that **4a** might be

Table 2. Scope of the Palladium(II) Acetate Catalyzed Tandem Cycloisomerization and Oxidation of Arylvinylcyclopropenes



entry[a]	1 ($R^1/R^2/R^3/R^4$)	2	yield[b] (%)
1	**1b** (H/4-CH_3/CH_3/CH_3)	**2a**, *p*-BQ	**3b**, 93
2	**1c** (H/4-Cl/CH_3/CH_3)	**2a**, *p*-BQ	**3c**, 99
3	**1d** (4-CH_3/H/CH_3/CH_3)	**2a**, *p*-BQ	**3d**, 97
4	**1e** (4-Cl/H/CH_3/CH_3)	**2a**, *p*-BQ	**3e**, 92
5	**1f** (H/3-Cl/CH_3/CH_3)	**2a**, *p*-BQ	**3f**, 85[c]
6	**1g** (H/2-Cl/CH_3/CH_3)	**2a**, *p*-BQ	**3g**, 86 (93)[d,e]
7	**1h** (H/4-Br/CH_3/CH_3)	**2a**, *p*-BQ	**3h**, 83
8	**1i** (H/H/$-(CH_2)_5-$)	**2a**, *p*-BQ	**3i**, 36 (70)[e]
9	**1j** (H/H/CH_3/H)	**2a**, *p*-BQ	**3j**, 84[f]
10	**1k** (H/H/H/H)	**2a**, *p*-BQ	**3k**, 71[f]
11	**1a**	**2b**, DDQ	complex products
12	**1a**	**2c**, 2,3,5,6-tetramethyl-1,4-BQ	–

[a] Unless otherwise specified, all reactions were carried out using **1** (0 0.2 mmol) and **2** (0.4 mmol) in the presence of $Pd(OAc)_2$ (0 0.0 1 mmol) in THF (2 0.0 mL) at 50 °C for 24 h. [b] Isolated yields. [c] Ratio of two isomers is 1:1, determined by ^1H NMR spectroscopic data. [d] Reaction was carried out at 70 °C for 36 h. [e] Values in brackets: yields based on the recovered starting materials. [f] Reaction was carried out at 40 °C for 48 h.

transformed from **3a** via the elimination of *p*-hydroquinone. Increasing the amount of catalyst to 1.0 equiv impaired the reaction outcome, affording **3a** in lower yields (Table 1, entries 3 and 4). Under aerobic conditions, **3a** was only produced in 5% yield in the absence of acetic acid (Table 1, entry 5). Further examination of the additive and solvent effects revealed that water is the best additive and THF is the solvent of choice for this transformation (Table 1, entries 6−11). Examination of other Pd catalyst sources indicated they are not suitable for this reaction, and stoichiometric

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(7) (a) Bäckvall, J. E.; Nordberg, R. E. *J. Am. Chem. Soc.* **1981**, *103*, 4959. (b) Bäckvall, J. E.; Awasthi, A. K.; Renko, Z. D. *J. Am. Chem. Soc.* **1987**, *109*, 4750. (c) Bäckvall, J. E.; Hopkins, R. B.; Grennberg, H.; Mader, M. M.; Awasthi, A. K. *J. Am. Chem. Soc.* **1990**, *112*, 5160. (d) Grennberg, H.; Gogoll, A.; Bäckvall, J. E. *Organometallics* **1993**, *12*, 1790. (e) Grennberg, H.; Bäckvall, J. E. *Chem.−Eur. J.* **1998**, *4*, 1083. (f) Jonasson, C.; Karstens, W. F. J.; Hiemstra, H.; Bäckvall, J. E. *Tetrahedron Lett.* **2000**, *41*, 1619.

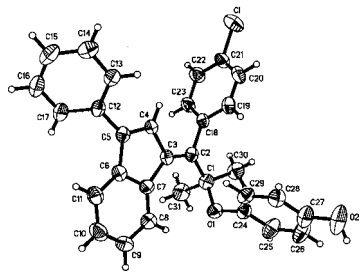
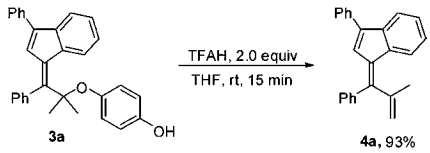


Figure 1. ORTEP drawing of compound **3c**.

Pd(0)/*p*-hydroquinone is required to promote this reaction, giving **3a** in 52% yield under otherwise identical conditions (Table 1, entries 12−14). With the addition of TEMPO (2.0 equiv), the reaction proceeded smoothly, rendering unlikely the intervention of a radical pathway (Table 1, entry 15). It should be also noted the reaction cannot take place in the absence of a Pd catalyst (Table 1, entry 16).

We further validated that **4a** was derived from **3a**. In the presence of excess trifluoroacetic acid (TFAH), adduct **3a** can be easily converted to **4a** in 93% yield within 15 min at 20 °C (Scheme 1).[7d]

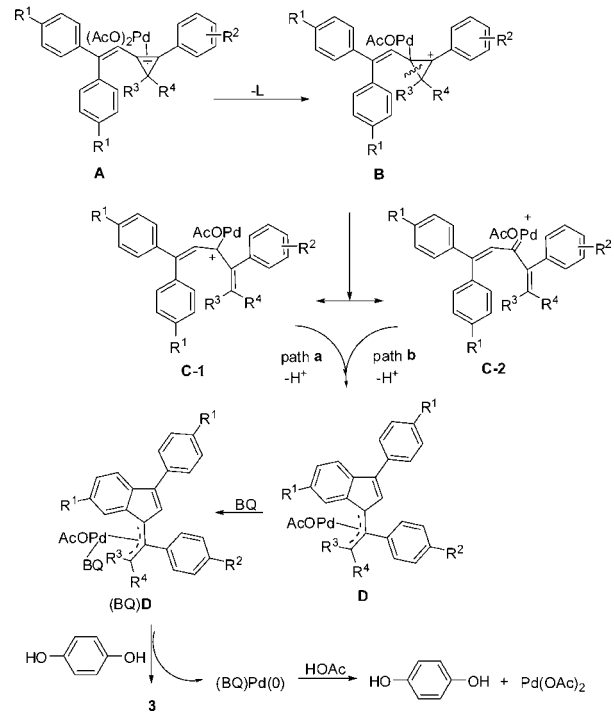
Scheme 1. Acid-Promoted Dehydroquinonation of Adduct **3a**



We next examined a variety of arylvinylcyclopropenes **1** and benzoquinones **2b** and **2c** in this reaction, and the results are shown in Table 2. As can be seen from Table 2, the reactions took place smoothly with various electron-withdrawing or -donating substituents on the benzene rings of arylvinylcyclopropenes **1b**−**1h**, affording the corresponding products **3b**−**3h** in excellent yields (Table 2, entries 1−7). Meanwhile, it should be also noted that the substitution at the *meta* position on the R^2 ring slightly retarded the reaction (Table 2, entry 5), and higher reaction temperature as well as longer reaction time was required for the *ortho*-substituted **1g** (Table 2, entry 6). Bromo-substituted **1h** could also produce the corresponding adduct **3h** in 83% yield under the standard conditions without formation of any cross-coupling products (Table 2, entry 7). Sterically hindered cyclopropene **1i** strongly retarded the reaction, giving **3i** in 36% yield under the standard conditions (Table 2, entry 8). Tri- or disubstituted arylvinylcyclopropenes **1j** (R^3 or R^4 = H) and **1k** (R^3 and R^4 = H) also tolerated the standard reaction conditions, producing the corresponding products **3j** and **3k** in 84 and 71% yield, respectively, at 40 °C for 48 h (Table 2, entries 9 and 10). However, other BQs such as 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ, **2b**) or 2,3,5,6-tetramethyl-1,4-BQ (**2c**) are not suitable oxidant and pro-nucleophile to this reaction (Table 2, entries 11 and 12). Additionally, we added 2 equiv of external oxygen-containing nucleophiles (LiOAc, methanol, or phenol) in the reactions using cyclopropene **1a** as the substrate under the standard conditions. It was found that methyleneindene derivative **3** was isolated in >90% yield exclusively in each case. When using diphenethylamine or benzylamine as the external nucleophiles, we only recovered starting materials **1**. The in situ generated nucleophilic hydroquinone could be crucial for this reaction.

A plausible mechanism for the formation of these methyleneindene derivatives is outlined in Scheme 2. Activation

Scheme 2. Plausible Reaction Mechanism



(8) For other pathways of oxidation of cyclopropenes (e.g., hydroboration and oxidation of cyclopropenes), see: (a) Köster, R.; Aurora, S.; Binger, P. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 205. (b) Zimmerman, H. E.; Nuss, J. M.; Tantillo, A. W. *J. Org. Chem.* **1988**, *53*, 3792. (c) Rubin, M. A.; Baird, M. S.; Bolesov, I. G. *Zh. Org. Khim.* **1997**, *33*, 966. (d) Rubina, M.; Rubin, M.; Gevorgyan, V. *J. Am. Chem. Soc.* **2003**, *125*, 7198.

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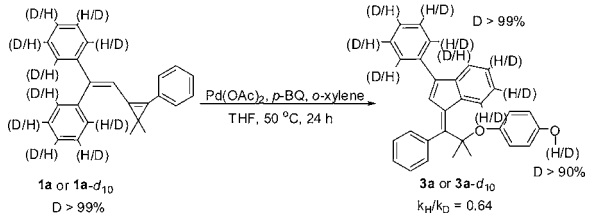
of cyclopropene **1** by Pd(II) forms intermediate **A**, which can produce intermediate **B**. Since the intramolecular rearrangement forming naphthalene derivative was not observed, we believe that the mechanism on the formation of **B** is very similar to that of $Cu(OTf)_2$-catalyzed rearrangement of arylvinylcyclopropenes **1**.[12a] Ring opening of intermediate **B** produces cationic intermediate **C-1** as well as the corresponding palladium carbene intermediate **C-2**,[14] which undergoes intramolecular Friedel−Crafts reaction or carbene insertion of an aromatic C−H bond to form π-allyl palladium intermediate **D**. In this step, the cyclized aromatic ring of R^1 and aromatic ring of R^2 are located at the opposite side of the π-allyl palladium intermediate presumably due to the steric hindrance of R^1 and R^2 aromatic rings. To verify the existence of carbene intermediates, we carried out a deuterium labeling experiment using **1a**-d_{10} as the substrate under the standard conditions (without addition of H_2O to avoid the interference of additional proton source) to examine the isotope effect of the reaction (Scheme 3; for the details, see

Scheme 3. Deuterium Labeling Experiment in the Palladium(II) Acetate Catalyzed Tandem Cycloisomerization and Oxidation of Arylvinylcyclopropenes **1a** and **1a**-d_{10}



the Supporting Information). It was found that using **1a**-d_{10} as the starting materials a kinetic isotope effect $k_H/k_D \approx 0.64$ was observed along with the phenolic hydroxyl group having D content >90%. Since the generally reported C−H insertions by metal carbene have $k_H/k_D \approx 1.6-4.2$ kinetic isotope effect,[15] the carbene intermediate in this reaction is perhaps not as the main intermediate. Therefore, the intramolecular Friedel−Crafts reaction might be a major process in this reaction.[16] After external attack of *p*-BQ coordinated intermediate **D**[17] by the hydroquinone, product **3** is formed exclusively in *Z*-configuration and a (BQ)Pd(0) complex is formed that reacts with acetic acid to give $Pd(OAc)_2$ and hydroquinone[7d] (*p*-BQ is an oxidant and a pro-nucleophile). The yield of **3** increased after adding some water presumably due to the contribution of H^+ transfer in the system by H_2O via H_3O^+ species. We also found that during the first 3 h of the reaction **3** was almost not formed, suggesting that an induction period is required. This may be because the initial nucleophile *p*-hydroquinone is generated slightly via oxidation of a small amount of Pd(0)[18] in the system by *p*-BQ to accomplish the catalytic cycle (see the Supporting Information).

We have developed an unusual tandem cycloisomerization and oxidation reaction of arylvinylcyclopropenes catalyzed by Pd(II) acetate with *p*-BQ as oxidant and pro-nucleophile. This synthetic protocol furnishes methyleneindene derivatives straightforwardly from simple starting materials in good to excellent yields under mild conditions, substantially enriching the Pd(II)/Pd(0)−benzoquinone/hydroquinone redox system. A plausible mechanism has also been proposed that is based on an intramolecular Friedel−Crafts reaction or carbene insertion pathway. Clarification of the reaction mechanism and further application of this chemistry are in progress.

Acknowledgment. We thank the Shanghai Municipal Committee of Science and Technology (06XD14005 and 08dj1400100-2), National Basic Research Program of China (973)-2009CB825300, and the National Natural Science Foundation of China for financial support (20872162, 20672127, 20732008, 20821002, and 20702013), and Mr. Jie Sun in State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, for performing X-ray diffraction.

Supporting Information Available: Experimental procedures, full characterization of new compounds shown in Tables 1 and 2, and X-ray crystal analysis data of **3c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) The crystal data of **3c** have been deposited in CCDC with number 729852. Empirical formula: $C_{36}H_{37}ClO_5$; formula weight = 585.11; crystal color, habit = colorless, prismatic; crystal dimensions = 0.397 × 0.369 × 0.203 mm; crystal system = rhombohedral; lattice type = primitive; lattice parameters = a = 30.1433(15) Å, b = 30.1433(15) Å, c = 18.809(3) Å, a = 90°, b = 90°, γ = 120°, V = 14081(2)Å^3; space group $R\bar{3}$; Z = 18; D_{calc} = 1.182 g/cm^3; F_{000} = 5580; diffractometer = Rigaku AFC7R; residuals R; Rw 0.0815, 0.2467.

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(16) Most of the Friedel−Crafts reactions exhibit inverse isotope effects (k_H/k_D < 1, ~0.8−0.9). See: (a) Melander, L. *Isotope Effect on Reaction Rates*; Ronald Press: New York, 1960; pp 107−123. (b) Anslyn, E. V.; Dougherty, D. A. *Modern Physical Organic Chemistry*; University Science Books: Mill Valley, CA, 2006; pp 428−431.

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