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PALLADIUM-CATALYZED OXIDATIVE COUPLING OF AROMATIC COMPOUNDS WITH OLEFINS USING t-BUTYL PERBENZOATE AS A HYDROGEN ACCEPTER

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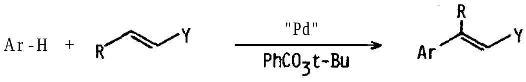
Abstract—Benzene and furans undergo oxidative coupling with olefins with an aid of t-butyl perbenzoate and a catalytic amount of Pd salts. The perbenzoate acts as a hydrogen accepter. In the absence of olefins, Pd catalyzed benzoxylation of aromatic compounds takes place.

One interesting feature of Pd chemistry is a facile reduction of di-valent Pd to zero-valent state accompanied by oxidation of a wide variety of organic molecules.' For example, an intermolecular dehydrogenation reaction between water and olefins produces the corresponding ketones or aldehydes during the reduction of $PdCl_2$ to Pd black.* The ingenious discovery that $CuCl_2$ under oxygen atmosphere regenerates *in situ* the active Pd(II) species led to establish the famous industrial process of producing acetaldehyde from ethylene, so-called the Wacker process.[3] Resides $CuCl_2$, other oxidants such as nitric acid[4] and *p*-benzoquinone[5] are used as reoxidants of the reduced Pd.

As another intermolecular dehydrogenation reaction, Moritani *et al.* reported that aromatic compounds underwent oxidative coupling with olefins to give styryl derivatives during the reduction of $Pd(OAc)_2$.[6] In this case, too, much effort has been made to carry out the reaction with a catalytic amount of $Pd(OAc)_2$ by adding appropriate reoxidants of Pd(O), however, the turn-over number was not high. For example, in the reaction of benzene with styrene, the turn-over number was lower than five using molecular oxygen,[7] Ag salt,* or Cu salt under oxygen atmosphere.* In the reactions of furans with acrylates, relatively higher turn-over was observed, but little more than twenty.' The results are sharp contrast extremely high turn-over observed in the oxidation of olefins with Pd-Cu catalyst system.'

In our continuous effort to elucidate the scope and limitation of Pd-mediated oxidations, we have found that Pd-catalyzed oxidation of olefins to ketones proceeded in the presence of hydrogen peroxide or t-butyl hydroperoxide.[10] The new system was especially effective to the oxidation of a,/?-unsaturated esters or ketones to *β*-keto esters or *β*-diketones, respectively.[10] One explanation of this result is the oxidation of olefins with Pd(II), followed by the reoxidation of the reduced Pd with hydroperoxides. On the other hand, Mimoun *et al.* independently reported the oxidation of olefins with a combination of Pd salts and hydroperoxides, claiming that an essential step of the oxidation is formation of PdOOR species and the successive oxygen transfer to olefins." According to their mechanism, neither oxidation nor reduction of Pd is involved in the catalytic cycle.

In this paper, we wish to report the oxidative coupling of benzene or furans with olefins using t-butyl perbenzoate and lower than 5 mol% of Pd salts, and to discuss the mechanism of Pd-catalyzed oxidation in the presence of peroxide derivatives.



Scheme 1.

RESULTS AND DISCUSSION

Moritani *et al.* carried out oxidative coupling of benzene with olefins using $Pd(OAc)_2$ in acetic acid.[6] We first attempted to make the reaction catalytic by adding hydroperoxides or dialkyl peroxides as the reoxidant of Pd(0). However, regeneration of Pd(II) species was not possible with hydrogen peroxide, t-butyl hydroperoxide, or di-t-butyl peroxide. Dibenzoyl peroxide showed a little activity, but considerable amounts of biphenyl and other by-products were formed.

Satisfactory catalytic reaction was accomplished by using t-butyl perbenzoate. Heating an acetic acid solution of olefin and excess benzene at 100° for 3-5 hr afforded the corresponding styryl derivatives in the presence of t-butyl perbenzoate (equivalent to the olefin) and a catalytic amount of $Pd(OCOR)_2$ (R = Me, Ph). The turn-over numbers were 10-14, which are higher than those reported in the literature with other reoxidants.[7,8] In acetonitrile, THF, or ethyl acetate, instead of acetic acid, yields of the corresponding products were lower. As the olefin, *α,β*-unsaturated esters, ketones, and even aldehydes were used, and the aryl group was always introduced at the /I-position of the carbonyl group. The results are summarized in Table 1. Olefins without electron-withdrawing substituents were scarcely coupled with benzene in acetic acid, the main course. of the reaction being Pd-promoted oxidative acetoxylation of the olefins. Substituted benzenes such as chlorobenzene and toluene also underwent the Pd-catalyzed coupling with olefins in the presence of t-butyl

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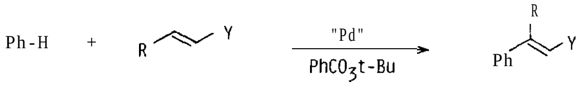
Table 1. Oxidative coupling of benzene with olefins[a]



	R	Y	Yields(%)	
1.	Ph	COMe	65	(1)
2.	Ph	CHO	64	(2)
3.	Me	CHO	48$^{b)}$	(3)
4.	H	CO_2Me	70$^{c)}$	(4)
5.	Ph	CO_2Me	56	(4)

a) All reactions were carried out in acetic acid at 100°C for 3 h in the presence of $Pd(OCOPh)_2$ (5 mol%) and t-butyl perbenzoate (100 mol%). An equimolar amount of olefin to the perester and excess of benzene were employed. The yields were calculated based on the olefin.

b) A mixture of E and Z isomers was obtained.

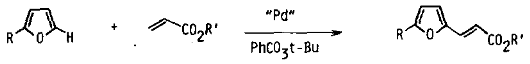
c) Two molar excesses of the pa-ester to olefin were used, and methyl β,β-diphenylacrylate (4) was obtained. when an equimolar amount of the perester was used, a mixture of methyl cinnamate and 4 was obtained.

perbenzoate. However, the reaction was not regioselective and gave a mixture of *o*-, *m*-, and p-substituted isomers.

The reaction of furan with olefins is known to be faster than that of benzene.[6,9] The same tendency was observed in the catalytic reaction promoted by t-butyl perbenzoate. In the presence of 1 mol% of $Pd(OCOPh)_2$, the coupling products were obtained in high ‘yields within 3 hr. We chose methyl or ethyl acrylate, and carried out the reaction of various furans. The results are summarized in Table 2. The turn-over numbers were higher than 35, which are twice as high as those reported by Fujiwara et *al.* using $Cu(OAc)_2$ under oxygen atmosphere as the reoxidant.[9] Furthermore, selectivity of the reaction was very high, and the products produced from two moles of furans and one mole of olefins, or one mole of furans and two moles of olefins, were not detected. The olefinic bond of the product was exclusively trans in all cases. In the reaction of 2-substituted furans bearing either an electron-withdrawing group or electron-donating group, the coupling took place at 5-position.

In these reactions, it was confirmed by GLC analysis that the perester was converted to equimolar amounts of benzoic acid and t-butyl alcohol; the perester acts as hydrogen accepter in the reaction. Since the oxidative coupling of aromatic as well as heteroaromatic compounds with olefins is a characteristic reaction of divalent Pd, it seems reasonable that the perester reoxidizes Pd(0) in the catalytic cycle. However, it should be taken into account that certain radical species which can be induced by thermal decomposition of the perester might be in-

Table 2. Oxidative coupling of furans with acrylates[a]



	R	R'	Yields(%)	
1.	H	Et	53	(5)
2.	Me	Et	67	(6)
3.	CHO	Me	34	(7)

a) All reactions were carried out in acetic acid at 100°C for 3 h in the presence of $Pd(OCOPh)_2$ (1 mol%) and t-butyl perbenzoate (100 mol%). Equimolar amounts of furan, acrylate, and the perester were employed. The yields were determined based on the olefin.

volved in the reaction." In order to obtain further information on the Mechanism, we carried out a controlled experiment in the absence of olefins.

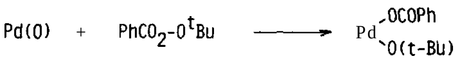
A benzene solution of t-butyl perbenzoate and 1 mol% of **Pd(OCOPh)$_2$** was heated at 100° for 3 hr to give a mixture of phenyl benzoate, diphenyl, and benzoic acid in 24, 4 and 55% yields, respectively. Presence of ligands bipyridine or triphenylphosphine did not affect the yields or distribution of the products. Addition of solvents such as acetic acid and THF led to selective formation of benzoic acid. The product distribution was dependent on the catalyst; use of **Pd(OAc)$_2$, PdCl$_2$(PhCN)$_2$, PdCl$_2$(PPh$_3$)$_2$,** or **Pd(PPh$_3$)$_4$** afforded the products in a similar ratio to that with **Pd(OCOPh)$_2$,** whereas little phenyl benzoate was obtained with **PdCl$_2$** or **Pd/C**.

A similar reaction proceeded in substituted benzenes. In toluene, a mixture of benzyl benzoate, *o*-, *m*-, and p-tolyl benzoates was obtained in 39% combined yield in a ratio of 5:46: 34: 11. Small amounts of bitolyl and bibenzyl accompanied with benzoic acid were also detected. In chlorobenzene, *o*-, m-, and p-chlorophenyl benzoates were obtained in 26% combined yield in a ratio of 6: 48 :46, accompanied by the homo-coupling products and benzoic acid.

$$\text{Ar-H} + \text{PhCO}_3\text{t-Bu} \xrightarrow{\text{"Pd"}} \text{ArOCOPh} + \text{t-BuOH}$$

Scheme 2.

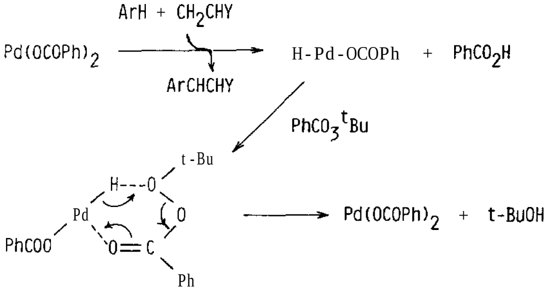
Above results can be explained by both radical mechanism and Pd-mediated mechanism. It is known that benzoxyl radical is easily generated by Cu-catalyzed reaction of dibenzoyl peroxide, leading to aromatic benzoxylation.[13] On the other hand, reduction of **Pd(OAc)$_2$** in acetic acid with aromatic compounds affords a mixture of biaryl and aryl acetate.[14] However, the participation of radical species can be excluded by isomer distribution observed in the reaction of substituted benzene. In the radical reaction, chlorobenzene and toluene afforded o-benzoxylation preferentially. While, in the Pd-promoted oxidation, *m*-and *p*-isomers were obtained as main products. In the catalytic reaction presented in this paper, the product distribution was similar to that observed with a stoichiometric amount of **Pd(OAc)$_2$** in the acetoxylation of benzene derivatives. Thus, it is reasonable that the reaction is governed by redox of Pd and the perester plays a role in reoxidant of Pd(O), as shown in Scheme 3.



$$\text{Pd(O)} + \text{PhCO}_2\text{-O}^t\text{Bu} \longrightarrow \text{Pd}\genfrac{}{}{0pt}{}{\text{OCOPh}}{\text{O(t-Bu)}}$$

Scheme 4.

Mechanism of the reoxidation is not clear, but we wish to propose the following two explanations. One is oxidative addition of the perester onto **Pd(0)** involving O–O bond cleavage (Scheme 4). With some Ni or Cr complexes, a similar oxidative addition of peroxide derivatives has been reported.[15,16] Another one is direct oxidation of Pd-H species with the perester via a 6-membered cyclic transition state as shown in Scheme 5. In this case, O-O bond cleavage is also essential. With both mechanisms, **Pd(II) carboxylate** or related species is regenerated from the reduced zero-valent Pd species. In the Pd-mediated aromatic oxidations,[6,14] active Pd species are often limited to Pd carboxylates, and the difficulty to regenerate Pd carboxylates seems to cause rather inefficient catalytic reaction. The combination of Pd with peresters would be a good method to regenerate Pd-carboxylate species or its analogues in the catalytic cycle.

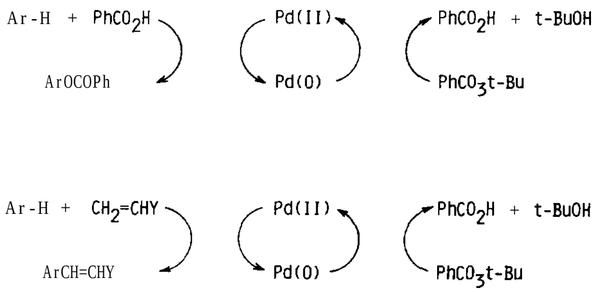


Scheme 5.

CONCLUSIONS

As described above, a new system, **Pd(OCOPh)$_2$** combined with t-butyl perbenzoate, leads to effective catalytic oxidative coupling of aromatic compounds with olefins. Since t-butyl perbenzoate is stable and can be handled with ease, the reaction is useful as a unique method to introduce certain alkyl substituents to aromatic rings.

As for the mechanism, we postulated the O-O bond cleavage by reduced Pd to regenerate **Pd(II)**



Scheme 3.

species. This hypothesis may be extended to the mechanism of Pd catalyzed oxidation of olefins with hydroperoxides. Minoun's explanation involving **PdOOR** species is clearly supported by the isolation and reactions of **RCOO-Pd-OO^{t}Bu** species,” but the possibility that the catalytic reaction involving reduction of Pd and **reoxidation** of the reduced Pd with hydroperoxides with O-O bond cleavage makes the catalytic cycle complete should not be excluded.

EXPERIMENTAL

General. All products are known in the literature, and they were identified by comparing m.ps and NMR and IR spectra with the reported data as shown below. **4,4-Diphenylbuten-2-one 1**: mp of **2,4-dinitrophenylhydrazone. 152.5–154°** (lit. **152–153°).**[17] 3-Phenylcinnamaldehyde **(2)**, m.p. of **2,4-dinitrophenylhydrazone**, 207.5” (lit. **205–206°).**[18] 3-Methylcinnamaldehyde **(3)**, m.p. of **2,4-dinitrophenylhydrazone**, isomer 1, **189°**, isomer 2, **218–219°** (lit. mixture of the isomers, **200–202°).**[18] Methyl **3-phenylcinnamate (4), m.p.** of the free acid after hydrolysis, 162-163” (lit. **161–163°).**[19] Ethyl **3-(2-furyl)acrylate (5)**, NMR and IR spectra were identical with the reported **data.**[20] Ethyl **3-(5-methyl-2-furyl)acrylate (6)**, NMR spectrum was identical with the reported data.[21] Methyl **3-(5-formyl-2-furyl)-**acrylate **(7)**, m.p. 106-107” (lit. **106.5°).**[22]

General procedure for the oxidative coupling of benzene or furans with olefins. A mixture of **$Pd(OCOPh)_2$ (17 mg,** 0.05 mmol), t-butyl perbenzoate (194 mg, 1 mmol), benzene (I **mL)**, in **AcOH** (5 ml) was heated in a **pyrex** tube fitted with a screw cap at **100°** for 3 hr. The mixture was cooled, poured into cold water, and extracted with benzene. The combined extracts were washed with 10% **NaOH**, with cooling, and then with brine. The soln was dried over **$MgSO_4$** and concentrated. Purification of the residue by column chromatography **(n–hexane–ether**, silica-gel) gave the desired product. The reaction of furans was carried out in the same manner as above using 1 **mol%** of **$Pd(OCOPh)_2$** and 1 mmol of **furan**.

General procedure for benzoxylation of aromatic compounds. In a **pyrex** tube fitted with a screw cap, a mixture of benzene **(1 mL), $Pd(OCOPh)_2$** (3.5 mg, 0.01 mmol), and the **perester** (194 mg, 1 mmol) was heated at **90–100°** for 3-5 hr. After removal of the solvent, the residue was purified by column chromatography (silica-gel, **hexane–ether**). In the cases of toluene or chlorobenzene, 5 **mol%** of **$Pd(OCOPh)_2$** was employed, and the product distribution was determined by GLC.

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