

Palladium-catalyzed allylic acetoxylation of olefins using hydrogen peroxide as oxidant

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Received 2 January 1995; accepted 20 March 1995

Abstract

A new and efficient system for the allylic acetoxylation of olefins has been developed, which consists of a palladium (II) catalyst and hydrogen peroxide as oxidant in acetic acid. The acetoxylation reaction competes with the epoxidation by the peracetic acid generated in situ in this system. Increase of the concentration of palladium catalyst and addition of benzoquinone (BQ), enhance the acetoxylation considerably. For the Pd(OAc)₂-BQ-H₂O₂ system, more than 1000 turnover number could be achieved in the acetoxylation of cyclohexene. Most internal and cyclic olefins tested gave the corresponding allylic acetates in fair to high yields. 1,3-Cyclohexadiene gave 1,4-diacetoxy-cyclohex-2-ene while 1,5-hexadiene afforded 3-acetoxy-methylenecyclopentane; 1,7-octadiene produced 1-octen-7-one and octan-2,7-dione. Terminal olefins gave methyl ketones in good yield with high turnover number both in the presence and absence of BQ. Possible mechanisms and involvement of palladium peroxidic species in both the catalytic acetoxylation and ketonization of olefins are discussed.

Keywords: Acetoxylation; Allylic acetoxylation; Epoxidation; Hydrogen peroxide; Olefins; Palladium

1. Introduction

Methods for the allylic acetoxylation of olefins with palladium catalysts have been extensively studied because of the importance of allylic acetates as synthons for the fine chemical industry. Several catalytic systems such as Pd(OAc)₂-BQ-MnO₂, (BQ = benzoquinone), Pd(OAc)₂-BQ-ML-O₂, Pd(OAc)₂-Fe(NO₃)₃-O₂, and PdCl₂-AgOAc-TeO₂-^tBuOOH have been developed respectively [1], and their mechanism has been elucidated [2]. In these systems, continuous regeneration in situ of Pd(II) from PdH or Pd(0) by an oxidant is the key step for the efficient cat-

alytic oxidation, and in the case where BQ is used, multistep electron transfer systems are required. However, all these systems suffer from serious drawbacks such as low turnover numbers (TON) and complicated work-up procedures in the separation of the resulting acetates, which limit their application on an industrial scale.

As a strong, cheap and environmentally friendly oxidant, H₂O₂ is increasingly used in catalytic oxidations, and intensive studies to extend this area are being carried out worldwide [3]. A selective and efficient (selectivity > 90%, TON > 1000) method for oxidation of terminal olefins to methyl ketones using palladium carboxylates as catalysts and ROOH (R = H, ^tBu) as oxidants has been developed by one of the authors

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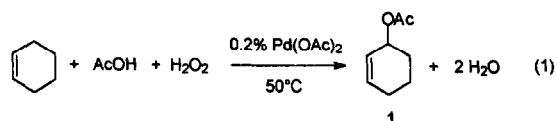
of this paper and his coworkers [4]. In this paper, we report on an efficient method for allylic acetoxylation of internal and cyclic olefins using H_2O_2 as oxidant and $\text{Pd}(\text{OAc})_2$ -BQ as catalyst, operating with high TON (in some cases > 1000) and easy work-up procedures. While this manuscript was in preparation, a similar system was described by Akermark et al. [5].

2. Results

Taking cyclohexene as a model to optimize the conditions, the allylic acetoxylation was carried out by the slow injection (> 2 h) of H_2O_2 (70% weight, 1.1 equiv.) to an AcOH solution of $\text{Pd}(\text{OAc})_2$ and the olefin at 50°C (molar ratio of olefin/Pd = 500). GC monitoring of the reaction using chlorobenzene as internal standard indicated the formation of 2-cyclohexenyl acetate **1** as the main product (72% conversion of cyclohexene, 80% selectivity) according to the Eq. (1) (Scheme 1).

The main by-product detected by GC/MS was *trans*-2-acetoxy-cyclohexanol **2** resulting from ring opening of cyclohexene epoxide by AcOH, formed by the reaction of the olefin with the peracetic acid generated in situ. Compound **2** was the main product in the absence of palladium catalyst, or even in the presence of palladium acetate (cyclohexene/Pd (mol) = 500) when peracetic acid was used as the oxidant, indicating that the acetoxylation reaction competes with the epoxidation. In addition, small amounts (< 3%) of cyclohexen-3-ol, cyclohexen-3-one and cyclohexanone were detected by GC/MS.

$\text{Pd}(\text{OAc})_2$ was the most efficient one among the catalysts listed in Table 1. $\text{Pd}(\text{PPh}_3)_4$ and Pd supported on silylated montmorillonite, which have been claimed to be superior catalysts for the ketonization of olefins [6], were found to be less selective than palladium acetate. $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ was also found to be less active, probably because chloride ions interfered with the acetoxylation reaction as previously reported [7].



Scheme 1.

The acetoxylation reaction was favored by relatively high concentration of $\text{Pd}(\text{OAc})_2$ (Fig. 1). For example, 82% selectivity in **1** with 72% conversion of cyclohexene was obtained at 1/500 of molar ratio of Pd/olefin. At lower concentration of $\text{Pd}(\text{OAc})_2$, the epoxidation increased at the expense of acetoxylation (e.g. 35% selectivity at Pd/olefin = 1/2000). It was also found that slow injection of H_2O_2 was necessary because its accumulation in the reaction medium resulted in a propensity to catalytic decomposition leading to Pd(0) precipitation, and to an increase in formation of peracetic acid at the same time and therefore of epoxidation by-products. For the same reason, high dilution was favorable for the acetoxylation. In order to obtain a homogeneous mixture,

Table 1
Effect of palladium catalyst on the allylic acetoxylation of cyclohexene with H_2O_2 as oxidant^a

Catalyst	Conversion (%)	Selectivity (%)
none	57	4
$\text{Pd}(\text{OAc})_2$	72	82
$\text{Pd}(\text{PPh}_3)_4$	40	41
$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$	60	42
Montmorillonite-Pd	49	50

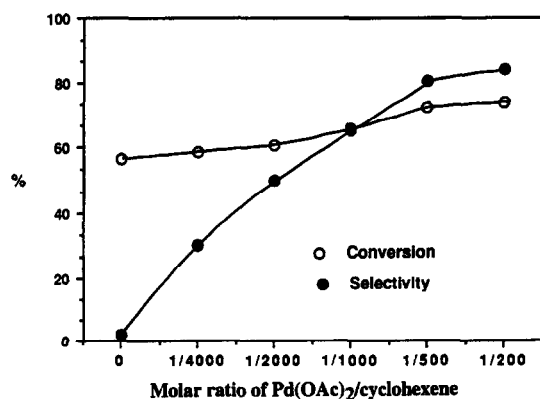
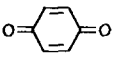
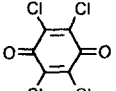
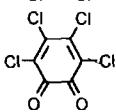
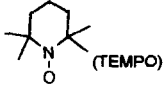

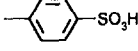


Fig. 1. Effect of the molar ratio of $\text{Pd}(\text{OAc})_2$ /cyclohexene on the conversion of cyclohexene and the selectivity of the allylic acetoxylation. Conditions: cyclohexene 2.0 g, HOAc 20 g, H_2O_2 (70%) 1.3 g, 50°C , 10 h including 3 h for the injection of H_2O_2 .

Table 2

Table 2 Effect of additives on the allylic acetoxylation of cyclohexene with H_2O_2 as oxidant catalyzed by $\text{Pd}(\text{OAc})_2$ ^a

Additive	Conversion(%)	Selectivity (%)
no	72	61
	80	93
	65	70
	63	62
 (TEMPO)	55	67
$\text{CH}_3\text{CONMe}_2$	58	35
	50	11
	69	45
CuCl_2	15	70

^a Conditions: cyclohexene 2.0 g, HOAc 20.0 g, H_2O_2 (70%) 1.1 eq., 10 h (including 3 h for the injection of H_2O_2), 50 °C, cyclohexene/ $\text{Pd}(\text{OAc})_2$ /Additive (mol)=1000/1/20.

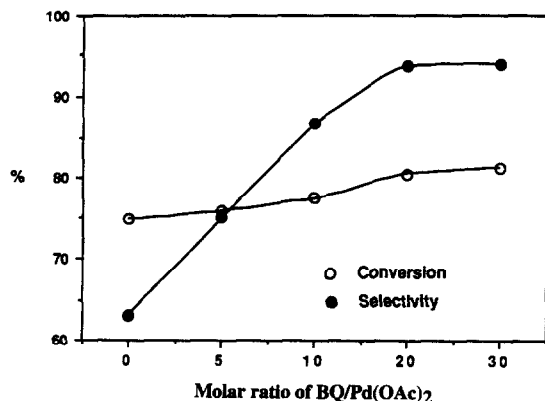


Fig. 2. Effect of the molar ratio of $\text{BQ}/\text{Pd}(\text{OAc})_2$ on the conversion of cyclohexene and the selectivity of the allylic acetoxylation. cyclohexene/ $\text{Pd}(\text{OAc})_2$ (mol) = 1000, BQ according to the ratios. Other conditions are as in Fig. 1.

commercially available 70% (weight) H_2O_2 instead of 35% was used as the oxidant.

Bases like *N,N*-dimethyl acetamide and pyridine which usually are used to slow down the peracid-mediated epoxidation [8], and strong acid like *p*-toluenesulfonic acid which has been claimed to accelerate the allylic acetoxylation [9], were found to favor the epoxidation instead of acetoxylation (Table 2). Presumably the bases may block the palladium catalysts [10], and strong acid may facilitate the formation of peracetic acid [3].

Several reoxidants such as quinones, TEMPO¹ and cupric chloride also were tested as additives to the acetoxylation system $\text{Pd}(\text{OAc})_2\text{-H}_2\text{O}_2$ as depicted in Table 2. Among the various quinones used in Table 2, BQ was found to be the most effective. CuCl_2 quickly decomposed H_2O_2 , thus was not suitable as co-catalyst. The effect of co-catalyst was so important (Table 2, Fig. 2 and Fig. 3) that even at very low concentration of palladium acetate (e.g. $\text{Pd}/\text{olefin} = 1/1000$), the addition of 20 mol equiv. of BQ per palladium resulted in an increase of the conversion and selectivity to 80% and 93% from 72% and 61%, respectively, compared with the reaction in the absence of BQ. Fig. 2 shows that the beneficial effect of BQ reaches its maximum for a molar ratio $\text{BQ}/\text{Pd} = 20$.

The allylic acetoxylation system $\text{Pd}(\text{OAc})_2/\text{H}_2\text{O}_2$ improved by the addition of BQ was extended to preparative scale for the synthesis of **1**, and the allylic acetate was obtained in good yield (Table 3). The $\text{Pd}(\text{OAc})_2\text{-BQ-H}_2\text{O}_2$ system was so efficient that even at extremely low concentration of palladium acetate (e.g., $\text{Pd}(\text{OAc})_2/\text{olefin}$ (mol) = 1/2000) the reaction also afforded such good yield (ca. 70%), selectivity (85%) and high turnover number (> 1000). It is worth mentioning that the work-up procedure was simplified by using H_2O_2 as oxidant, the resulting acetate was simply isolated by distillation in 95–98% purity.

¹ TEMPO = 2,2,6,6-tetramethyl 1-piperidinyloxy free radical.

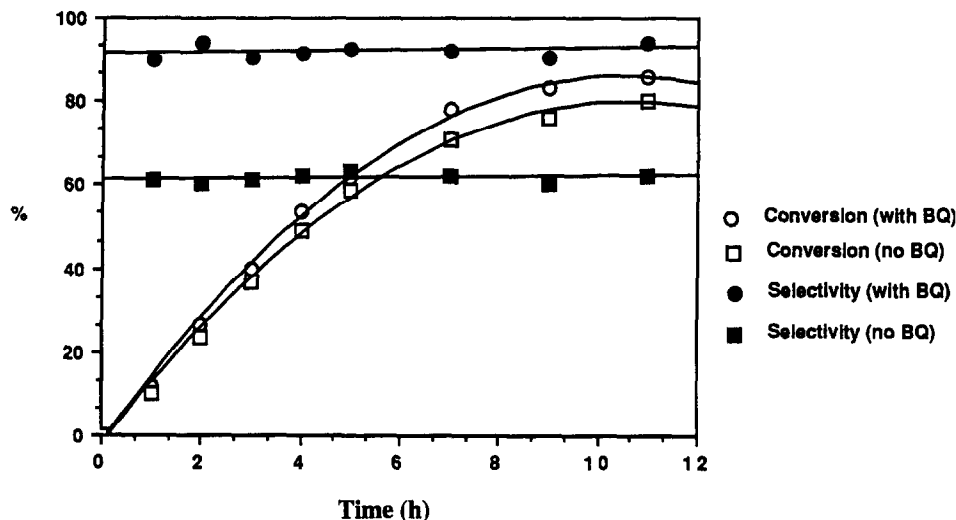


Fig. 3. Comparison of the time-dependent conversion and selectivity in the presence of BQ as co-catalyst (cyclohexene/Pd(OAc)₂/BQ = 1000/1/20) with those in the absence of BQ (cyclohexene/Pd(OAc)₂ = 1000). Other conditions are as in Fig. 1.

The Pd(OAc)₂-BQ-H₂O₂ system was also applied to the allylic acetoxylation of other cyclic and internal olefins as shown in Table 4. The structure of the olefins greatly influenced the activity and selectivity of the system. For a terminal olefin such as 1-octene, a methyl ketone, octan-2-one, was obtained in high yield, selectivity and TON as previously reported [4]. Most cyclic and internal olefins selectively gave the corresponding allylic acetates only at the relatively high concentration of palladium acetate (molar ratio of Pd/olefin = 1/500–1/33), while the corresponding epoxidation products were

formed as main products at very low concentration of palladium acetate (e.g. mol ratio of Pd/olefin = 1000, Table 4, run 1 and 4), even with dilute H₂O₂ (15%, Table 4, run 7). For some olefins, an appropriate concentration was necessary for the smooth preparation of the allylic acetate. For example, 2-cyclohexenyl acetate, 2-cyclopentenyl acetate and 2-cycloheptenyl acetate were synthesized respectively in good yield (64%, 60%, 55%) and selectivity (90%, 82%, 90%), at molar ratios of Pd/olefin = 1/1000, 1/500, 1/33 (Table 4, run 3, 2 and 6).

Palladium acetate plays a key role in the formation of allylic acetates in the competition with epoxidation. The main problem was the deactivation of the palladium catalyst caused by the partial precipitation at relatively high concentration, especially when the acetoxylation rate was slow. Improvement resulted when a small amount of activated carbon was added to the reaction system. The substituted cyclic olefin, 1-methyl cyclohexene gave 2-acetoxy-1-methyl cyclohexene as the main product. The internal olefin, 2-methyl 2-butene was converted to a mixture of two allylic acetates in good yield and selectivity (Table 4, run 11). In all cases, small amounts (1–5%) of the corresponding allylic ketones and ketones were found by GC/MS analysis.

Table 3

Table 3. Preparation of 2-cyclohexenyl acetate under optimized conditions^a

Cyclohexene / Pd / BQ (mol)	Conversion (%) GC	Yield (%) ^c		Selectivity (%)	
		GC	Isolated	GC	TON ^b
1000/1/20	72	61	50	85	610
1000/1/30	78	69	64	89	690
2000/1/80	84	72	65	85	1440
3000/1/180	85	49	/	57	1470







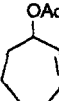






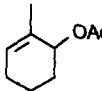


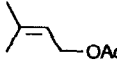
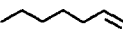

a. Conditions: cyclohexene 15 g, HOAc 150 g, 50 °C, 12–15 h (including 6 h for the injection of 70% H₂O₂, 1.1 eq.), BQ and Pd(OAc)₂ according to the ratio in the table.

b. Turnover number

c. Yield based on cyclohexene

Table 4

Table 4. Allylic acetoxylation of alkenes catalyzed by Pd(OAc)₂-BQ system with H₂O₂ as oxidant ^a

Run	Olefin	Olefin/Pd/BQ (mol)	Product and Yield (%) ^c	Selectivity (%)
1		1000/1/50	 20 ^d	40
2		500/1/35	 60	82
3		1000/1/30	 67	90
4		1000/1/50	 15 ^d	20
5		33/1/2	 47	78
6		33/1/2 ^b	55	90
7		1000/1/50 ^e	27	48
8		33/1/3	 12 ^d	48
9		33/1/3 ^b	 68	84
10		200/1/10 ^b	 33	74
11		100/1/4	 40	91
			 33	
12		1000/1/4	 69	94

a. Conditions: olefin 6 g, HOAc 60 g, 50 °C, 12–18 h (including 6 h for H₂O₂ injection), H₂O₂ 1.1 mol equivalent of olefin, Pd(OAc)₂ and BQ were added according to the ratio in the table.


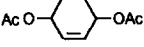



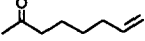
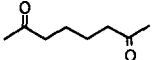




b. Activated carbon 0.5 g was added to the reaction system.

c. Isolated yield based on the olefin.

d. GC yield. e. H₂O₂ (15%)

Table 5

Table 5. The acetoxylation of dienes catalyzed by Pd(OAc)₂-BQ system with H₂O₂ as Oxidant ^a

Olefin	Products and Yield ^b	Selectivity (%)
 ^c	 65 Trans/cis=1	83
	 69	86
	 45	
	 14	
	 23	
	 13	
	low reactivity	

a. Reaction conditions: olefin 6 g, HOAc 80 g, Pd(OAc)₂ and BQ were added according to the mole ratio of olefin/Pd/BQ=100/1/3 12-18 h including 6 h for the injection of 70% H₂O₂, 1.1 eq., 50°C

b. Isolated yield based on the olefin.

c. Slow Injection (4 h) of 1,3-cyclohexadiene and H₂O₂ at the same time.

The oxidation system was also successfully used for the acetoxylation of dienes as indicated in Table 5. *trans*- and *cis*-1,4-Diacetoxy-2-cyclohexene were obtained from 1,3-cyclohexadiene by palladium-mediated 1,4-diacetoxylation in good yield (65%, *trans/cis*=1) and selectivity (83%). 1,5-Hexadiene gave 3-acetoxy-methylenecyclopentane as the main product (yield 69% and selectivity 86%) through palladium mediated annulation [11]. 1,7-Octadiene afforded 1-octen-7-one and octan-2,7-dione while 4-vinyl cyclohexene produced ketone

and acetate, respectively, from oxidation of the corresponding terminal and internal double bonds of the olefin.

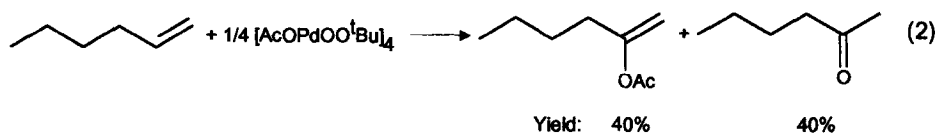
3. Discussion

The palladium-catalyzed acetoxylation of olefins using H₂O₂ as oxidant appears essentially as a metal-centered nucleophilic attack by two nucleophiles, i.e. H₂O₂ and AcOH on the olefin coordinated to palladium in a π or a π -allyl mode, in competition with a non metal-centered epoxidation of the olefin by the peracetic acid generated in situ. Thus the selectivity of the reaction is strongly dependent on the coordination mode (π or π -allyl), and the strength of the coordination of the olefins to palladium. A further aspect of this reaction stems from the ambivalent role of hydrogen peroxide which can oxidize olefin to ketone, reoxidize Pd(0) or Pd-H to Pd(II), or reoxidize hydroquinone to benzoquinone.

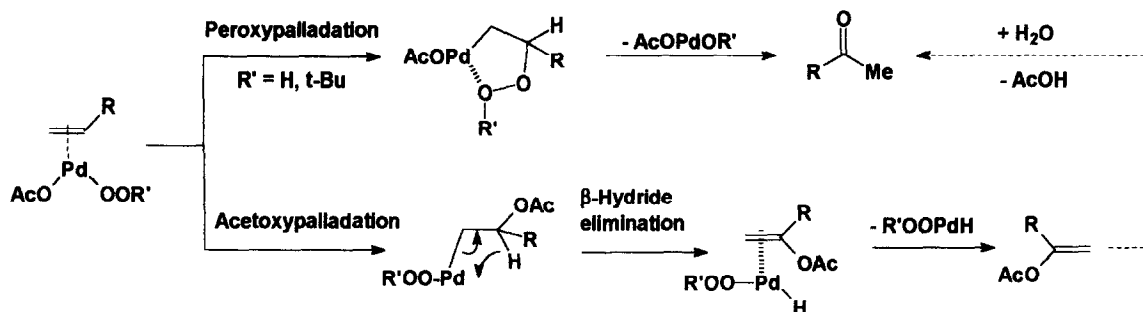
The stoichiometric oxidation of olefins by [AcOPdOO^tBu]₄, bearing both nucleophilic reactants involved in this study, may shed some light on the mechanism of the present oxidation.

3.1. Terminal olefins

Palladium peroxides [RCO₂PdOOR]₄ (R = H, ^tBu) have been proposed as intermediates in the catalytic ketonization of terminal olefins [4]. The stoichiometric reaction of [CF₃CO₂PdOO^tBu]₄ with terminal olefins has been shown to selectively give the corresponding methyl ketone through intramolecular peroxy-palladation of the coordinated olefin. The replacement of the electron-withdrawing and poorly nucleophilic trifluoroacetate group by the acetate anion resulted in the formation of a 50:50 mixture of 2-acetoxy-1-hexene and 2-hexanone for the stoichiometric oxi-



Scheme 2.



Scheme 3.

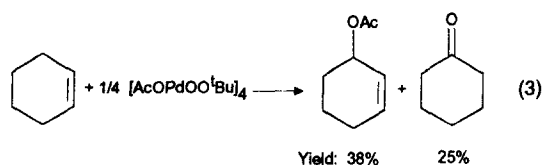
dation of 1-hexene by $[\text{AcOPdOO}^t\text{Bu}]_4$ (Eq. 2, Scheme 2) [4] (a).

As shown in Scheme 3, The formation of these two products results from the competitive Markovnikov acetoxypalladation- β -hydride elimination and peroxypalladation of the coordinated olefin, respectively. Under catalytic conditions, the oxidation of terminal olefins by H_2O_2 in AcOH mainly gives the corresponding methyl ketone both in the presence and absence of BQ, owing to the easy hydrolysis of the vinyl acetate to the methyl ketone in the presence of incipient water and that formed in situ.

3.2. Cyclic and internal olefins

The stoichiometric reaction of cyclohexene with $[\text{AcOPdOO}^t\text{Bu}]_4$ gave a 60:40 molar ratio of 2-cyclohexenyl acetate and cyclohexanone (Eq. 3, Scheme 4) implying that both acetoxypalladation- β -hydride elimination and peroxypalladation occur.

However, under catalytic conditions, the allylic acetoxylation is the dominant reaction both in the presence and absence of BQ, and the peroxypalladation products, i.e., the ketone and allylic ketone, are formed only in minor amounts. Whether the allylic acetoxylation under catalytic conditions results from an acetoxypalladation- β -hydride elimination (path a in Scheme 5), or both



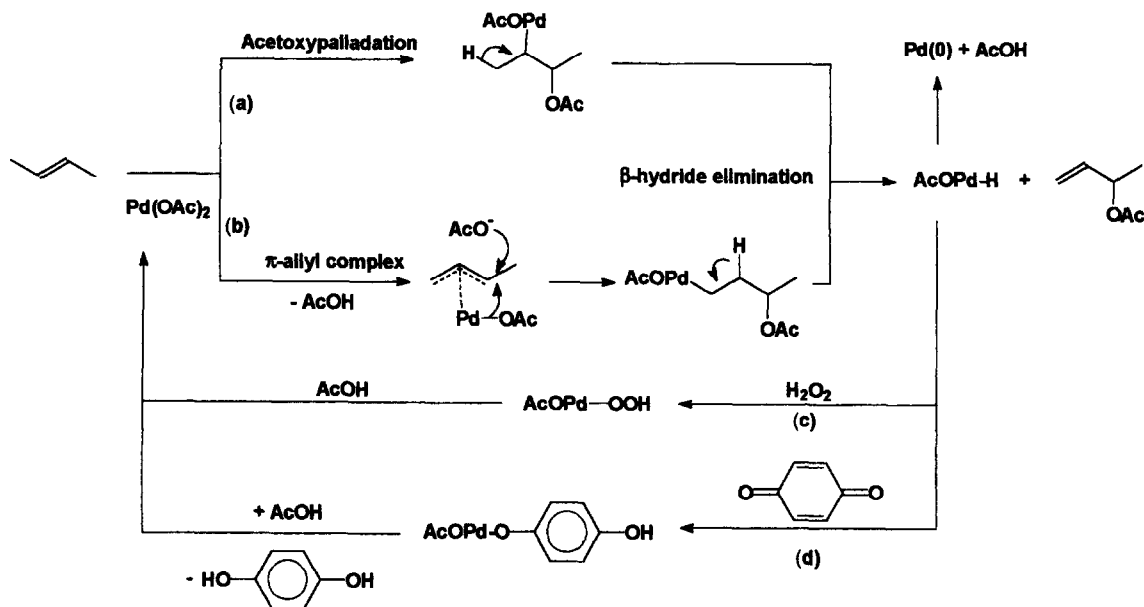
Scheme 4.

from external and intramolecular nucleophilic attack of acetate to the π -allyl intermediate (path b in Scheme 5), has long been a matter of debate [1], although recent isotopic studies by Bäckvall [2], Nicholas [12] and their co-workers support the π -allyl route (path b in Scheme 5). While the results of the stoichiometric oxidation imply that the former mechanism is possible, the later π -allyl route might be the main process operative under catalytic conditions. Also, the acetoxylation products in Table 4 and Table 5 may verify the later mechanism to some extent.

3.3. Reoxidation of Pd(0) or Pd-H species to Pd(II)

This is the key step in Wacker-type oxidations since it determines the turnover number and consequently the efficiency of the reaction. Although it is generally admitted that the resulting Pd(0) is reoxidized in situ to Pd(II) by Cu(II) or BQ through Pd-Cu [13] (b) or Pd(0)-BQ complexes [14], there is also considerable evidence to show that this reoxidation occurs at the Pd-H stage by formation of Pd(II) peroxidic species such as Pd-OOH by insertion of O_2 [13] (a) or reaction with H_2O_2 . Also, BQ which is vinylogous to O_2 , may well insert between the Pd-H bond as shown in Scheme 5.

Although there is a large positive effect of addition of BQ, the catalytic system has proven viable in the absence of BQ, suggesting that the Pd-H formed could be reoxidized by H_2O_2 (path c in Scheme 5), presumably via Pd-OOH species (Scheme 5). BQ as a reoxidant and ligand of palladium catalysts, prevents effectively the PdH



Scheme 5.

or Pd(0) from aggregation by the formation in situ of BQ–Pd complexes and transformation to Pd(II), and therefore considerably increases the efficiency of the acetoxylation. It was found in a separate experiment that hydroquinone was oxidized to BQ (42% yield and 56% conversion) by H_2O_2 (1.0 equiv.) in acetic acid at 50°C for 8 h (Eq. 4, Scheme 6).

So when BQ is involved, the whole multistep electron transfer system may be described as path d in Scheme 5, which Pd(II) is regenerated from PdH or Pd(0) by BQ, itself regenerated by H_2O_2 .

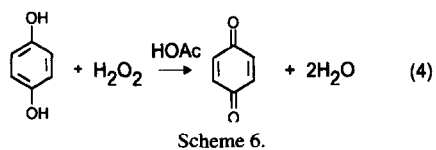
Activated carbon is a versatile reagent in palladium catalyzed reactions. It serves not only as a support to disperse and fix palladium [15], but also as an electron reservoir to the multielectron transfer reactions [16]. In some cases addition of activated carbon clearly improved the allylic acetoxylation (Table 4).

3.4. Competition between acetoxylation and epoxidation

The main side reaction, peracetic acid-mediated epoxidation, could be suppressed by control of the concentration of palladium acetate and addition of BQ, i.e., by acceleration of the allylic acetoxylation

(Table 3). The proper concentration of $\text{Pd}(\text{OAc})_2$ for the smooth preparation of allylic acetates depends largely on the structure of olefins, consequently on the rate of epoxidation and allylic acetoxylation.

The relative rate of the olefin epoxidation by peracetic acid has been reported to be in the order: cyclohexene (1.0) < cyclopentene (1.3) < cycloheptene (1.5) < cyclooctene 3.5 < internal olefin (10) < 1-alkyl cyclic olefin (17), etc. [17], while that of olefin acetoxylation estimated from the yield and reaction time by the $\text{Pd}(\text{OAc})_2$ –BQ– MnO_2 system [1] (a) is in the order: cyclopentene \approx cyclohexene > cycloheptene > internal olefin > cyclooctene. The olefin that exhibits the highest acetoxylation rate and the lowest epoxidation rate should be able to give the highest yield of the corresponding allylic acetate with the $\text{Pd}(\text{OAc})_2$ –BQ– H_2O_2 system. Cyclohexene, which conforms to these criteria, can be effectively converted to 2-cyclohexenyl acetate even at extremely low concentrations of palladium



Scheme 6.

acetate (e.g. molar ratio of Pd/cyclohexene = 1/2000) (Table 3).

Compared with other systems, the advantages of Pd(OAc)₂-BQ-H₂O₂ are obvious. Allylic acetates can be obtained from most olefins in good yield, selectivity and relatively high TON. H₂O₂, producing H₂O as the only side-product, simplifies the work-up process considerably. The resulting acetates are easily separated from the reaction mixtures by simple distillation. The system has potential for industrial application.

4. Experimental

4.1. Apparatus and chemicals

¹H NMR and ¹³C NMR spectra were recorded at 200 MHz using CDCl₃ as the solvent and SiMe₃ as internal standard. GC/MS was recorded on an Supelcowax 10 capillary column.

The solvents were purified and dried by standard methods. The olefins and most of chemicals otherwise indicated are commercially available and were used without further purification. Activated carbon (powder, ash < 1%) was purchased from Fluka. [AcOPdOO'Bu]₄ and Montmorillonite-Pd catalyst were respectively prepared according to the literature methods [4] (a), [6].

4.2. General procedure for acetoxylation of olefins catalyzed by palladium compounds with or without co-catalysts using H₂O₂ as oxidant

To a mixture of olefin, palladium catalyst, co-catalyst and HOAc, H₂O₂ (70% weight, 1.1 molar equivalent of olefin) was injected with stirring within 3–6 h at 50°C, and the reaction mixture was kept at the same temperature for 6–9 h. (Sometimes, activated carbon was added to the reaction system at the beginning of reaction.) After cooling the reaction mixture to room temperature, HOAc (ca. 90%) was removed under reduced pressure (35°C, 15 mmHg). The final acetate was isolated by distillation under reduced pressure with a 10 cm Vigreux column. (if the activated carbon was

added, the reaction mixture was filtered before removing HOAc).

If the reaction gave more than one product, flash column chromatography was used to separate them. All the acetates isolated were characterized with GC-MS, ¹H NMR and ¹³C NMR and the data were compared with those in the literature [1](a) [11,18]. The ratio of *trans*- to *cis*-1,4-diacetoxy 2-cyclohexene was determined by ¹H NMR [18] (b).

4.3. A typical example for the acetoxylation of olefins, preparation of 2-cyclohexenyl acetate

To a stirred mixture of cyclohexene (15 g, 182.9 mmol), AcOH (150 g), Pd(OAc)₂ (0.0410 g, 0.183 mmol) and BQ (0.592 g, 0.73 mmol), 70% (wt) H₂O₂ (9.8 g, 201.2 mmol) was introduced within 6 h at 50°C. The reaction mixture was kept at the same temperature for another 6 h. Then the reaction mixture was cooled to room temperature and the acetic acid was removed (ca. 90%) on a rotatory evaporator under reduced pressure (35°C, 15 mmHg). 2-cyclohexenyl acetate was finally isolated in 64.5% yield (16.5 g) and 97% purity by distillation with a 10 cm Vigreux column under vacuum (15 mmHg, 67–69°C). The structure of the acetate was confirmed by ¹H NMR, ¹³C NMR and GC-MS.

4.4. Oxidation of hydroquinone to BQ with H₂O₂

Under nitrogen atmosphere, H₂O₂ (70% weight, 1.0 equiv.) was introduced to a mixture of hydroquinone (0.50 g), chlorobenzene (0.1 ml, internal standard) and acetic acid (5 ml) within 2 h with stirring at 50°C. The reaction mixture was kept at the same temperature for 8 h. The final mixture was analyzed by GC and the products was identified by comparison with authentic samples. The oxidation gave benzoquinone in 42% yield with 56% conversion of hydroquinone.

4.5. Stoichiometric oxidation of cyclohexene by [AcOPdOO^tBu]₄

The reaction of [AcOPdOO^tBu]₄ with cyclohexene was carried out under nitrogen atmosphere. The similar procedure as the reaction of the palladium peroxide with 1-hexene [4] (a) was followed. The reaction gave 2-cyclohexenyl acetate and cyclohexanone in yields of 38% and 25%, respectively, based on the palladium peroxide.

Acknowledgements

We thank Firmenich S.A. for financial support of this work and for a postdoctoral fellowship (C.J.).

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