Journal of Organometallic Chemistry, 331 (1987) 113–119
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Palladium-catalyzed allylic oxidation of 1-(*p*-toluenesulfonyl)-2-propene and 1-(trimethylsilyl)-1-(*p*-toluenesulfonyl)-2-propene

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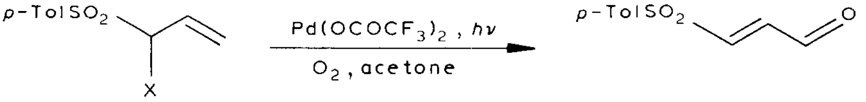
(Received February 18th, 1987)

Abstract

The course of palladium-catalyzed oxidation of a terminal alkene by t-BuOOH or by O_2/H_2O is greatly modified when the allylic carbon bears a *p*-toluenesulfonyl substituent, and allylic oxidation results. Mechanistic explanations of this observation are proposed.

Introduction

Allylic oxidation of alkenes is a matter of great practical importance and many approaches using transition metal complexes as catalysts have been developed [1]. We previously described the formation of α,β-unsaturated carbonyl compounds by UV irradiation of oxygenated solutions of η^3-allylpalladium complexes [2]. Direct allylic oxidation of alkenes in the presence of catalytic amounts of palladium salts was observed when the reaction mixture was irradiated under an oxygen atmosphere [3,4]; 1-(*p*-toluenesulfonyl)-1-propenal (**1**) was obtained in this way in good yield from either 1-(*p*-toluenesulfonyl)-2-propene (**2**) [4] or 1-(trimethylsilyl)-1-(*p*-toluenesulfonyl)-2-propene (**3**) [5], according to eq. 1. The best turnover numbers were obtained when the photoassisted reactions were carried out with $Pd(OCOCF_3)_2$ as catalyst and acetone as solvent, and thus we postulated the in situ formation of peroxidic derivatives of this solvent [3–5]. Such a hypothesis led us to examine the palladium-catalyzed oxidation of **2** and **3** in the absence of UV light either with anhydrous t-butylhydroperoxide instead of O_2/acetone/$h\nu$, or under conditions used for oxidation of terminal alkenes to methyl ketones [6].



(1)

(**2**: X = H;
3: X = SiMe$_3$)

(**1**)

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Table 1

Oxidation of **2** in the presence of $Pd(OCOCF_3)_2$ (0.07 equiv.) and anhydrous t-BuOOH (4 equiv.) at 50 ° C under argon

Run	Solvent	Time (days)	Conversion (%)	Selectivity [a] (%)		
				1	**4**	**5**
1	toluene	3	59	traces	39	22
2	toluene + NEt_3 (0.1 equiv.)	1	60	traces	17	5
3	acetone	1	58	—	18	—

[a] The selectivity corresponds to the isolated yield calculated by taking account of recovered starting material.

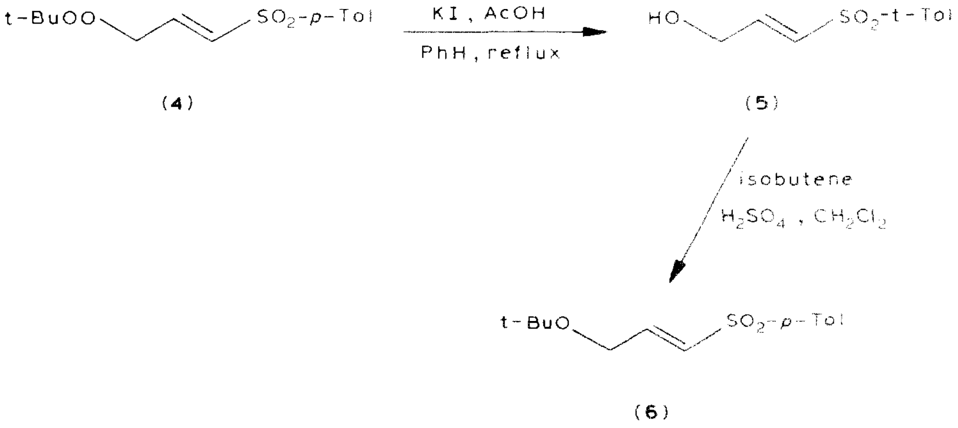
Results

(1) Allylic oxidation of 2 and 3 by t-butylhydroperoxide catalyzed by $Pd(OCOCF_3)_2$

When a toluene solution of the sulfone **2** was treated with anhydrous t-BuOOH (4 equiv.) and $Pd(OCOCF_3)_2$ (0.07 equiv.) no allylic oxidation was observed at room temperature. However, when the temperature was increased to 50 ° C, t-butyl peroxoether (**4**), allylic alcohol (**5**), and minute amounts of aldehyde **1** were obtained (Table 1, run 1).

Lower yields were obtained in the presence of triethylamine (run 2) or with acetone as solvent (run 3). Use of CuCl instead of $Pd(OCOCF_3)_2$ as catalyst did not give any **4** as was expected from reports in the literature [7,8]. When the sulfone **3** was used under similar conditions, the desilylated compound **2** was the major new product (conversion 65%; selectivity 55%), along with small quantities of oxidized products.

The structure of the peroxo compound **4** was established from its spectra, its reduction to the alcohol **5** by potassium iodide in the presence of acid [9], and the transformation of this alcohol into the t-butyl ether derivative **6** [10 *] (Scheme 1). Under the conditions of run 1, no alcohol **5** was formed from the peroxyether **4**.



Scheme 1

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* Reference number with asterisk indicates a note in the list of references.

Table 2

Oxidation of **2** and **3** at room temperature in aqueous dimethylformamide solutions ($DMF/H_2O = 7/1$)

Run	Starting material	$PdCl_2$ (equiv.)	Cocatalyst (equiv.)	Time (h)	Conversion (%)	Selectivity [a] (%)		
						5	**1**	**2**
4 [b]	**2**	0.1	CuCl (1)	20	36	10	35	
5 [b]	**2**	0.05	$(Me_2S)CuBr$ (2)	23	47	2	6	
6 [c]	**2**	0.01	benzoquinone (1.1)	20	35	8	16	
7 [b]	**3**	0.1	CuCl (1)	24	100	19	24	25
8 [b]	**3**	0.05	$(Me_2S)CuBr$ (2)	23	99	3	4	51
9 [c]	**3**	0.01	benzoquinone (1.1)	20	100	4	18	39

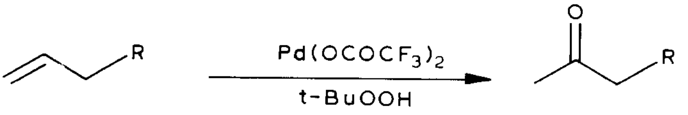
[a] cf. [a] in Table 1. [b] Reaction under oxygen (p 1 bar). [c] Reaction under argon.

2. *Allylic oxidation of **2** and **3** by oxygen and water catalyzed by $PdCl_2$*

When a solution of **2** in aqueous dimethylformamide ($DMF/H_2O = 7/1$) was treated with a palladium salt, the allylic alcohol **5** and the conjugated aldehyde **1** were formed (Table 2, runs 4–6). Under similar conditions, higher conversions were obtained from the α-silylated alkene **3** (runs 7–9) but the desilylated alkene **2** was the major product.

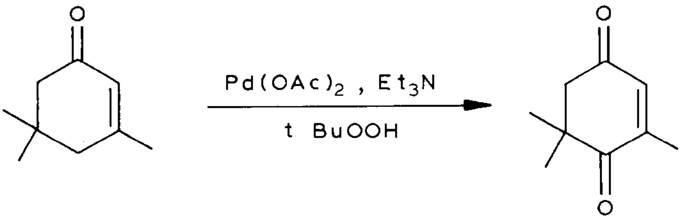
Discussion

The formation of an allylic alcohol, an allylic peroxyether, and a conjugated aldehyde in the oxidation of the sulfonylated alkenes **2** and **3** in the presence of Pd^{II} is very interesting in view of other reports *. A methyl ketone has been reported to be the main product of the oxidation of the palladium trifluoroacetate-catalyzed oxidation of terminal alkenes by t-butylhydroperoxide [12] (eq. 2), and a γ-diketone



(2)

was isolated from isophorone under fairly close conditions [14] (eq. 3). The formation of a methyl ketone by oxidation of terminal double bonds by $Pd^{II}/Cu^{II}/H_2O/O_2$ is a well known and useful reaction [6]; sometimes, the saturated aldehyde is isolated when the allylic carbon of the terminal alkene is substituted by an electron-withdrawing group [15].



(3)

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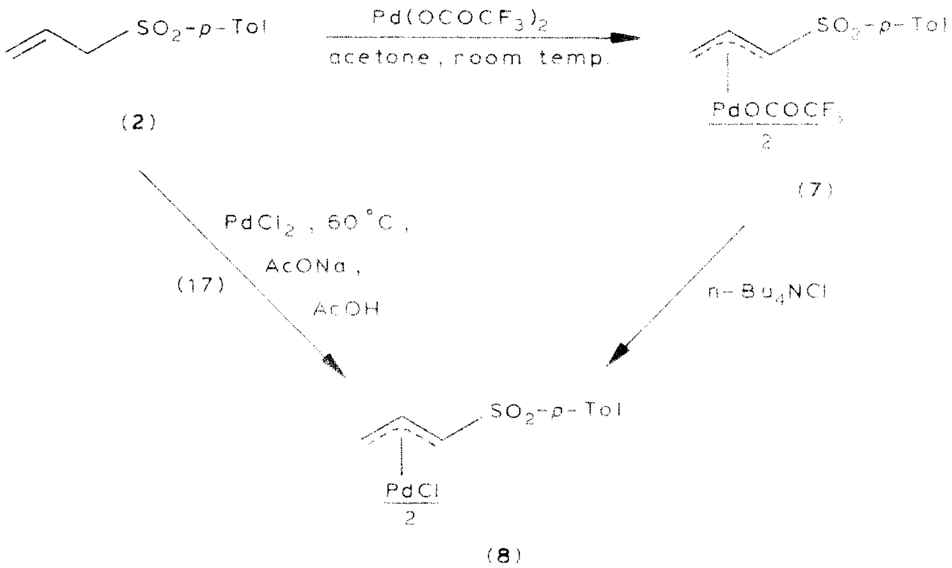
* Desilylation of **3** and **2** under our experimental conditions was unexpected and we cannot suggest a satisfactory explanation.



Scheme 2

In no case was formation of 1-(p-toluenesulfonyl)propan-2- (or -3)-one observed under our reaction conditions and it is evident that a p-toluenesulfonyl group has a great influence on both the selectivity and the mechanism of these oxidations. To our knowledge, this is the first palladium-catalyzed allylic oxidation of a terminal alkene by t-BuOOH or by H_2O/O_2 in the absence of UV light [1]. The mechanism of the oxidations reported in the present paper seems to depend on the reaction condition as shown below.

Although a η^3-allyl complex was postulated as an intermediate in the oxidation of isophorone shown in eq. 3 [13], literature reports show that t-butylhydroperoxide does not oxidise η^3-allylpalladium complexes [12,16]. We have confirmed that the t-butylperoxyether **4** is not obtained when a solution of η^3-allylpalladium complex **7** (Scheme 2) in toluene containing t-BuOOH is heated at 50 °C. Furthermore, **4** was not detected under radical conditions (CuCl/t-BuOOH, vide supra) [6,7]. On the basis of these facts participation of a η^2-olefin palladium intermediate A (Scheme 3) could be suggested, as proposed by Mimoun et al. [12,17] for the oxidation of terminal alkenes (eq. 2); after insertion of the double bond into the peroxy–Pd bond, the p-toluenesulfonyl group makes a β-elimination of Pd–H easier, and this leads to **4**. Formation of hydroxy compound **5** from intermediate C (Scheme 3) can be envisaged as involving rupture of the O–O bond and concomitant elimination of the t-BuOPdOCOCF$_3$ species, which in the presence of t-BuOOH gives the active catalyst t-BuOOPdOCOCF$_3$ [12].

For allylic oxidations brought about by $Pd^{II}/O_2/H_2O$, the decomposition of an η^3-allylpalladium intermediate such as **8** could be involved in the formation of **1** and **5** *. In fact, while this work was in progress, it was shown that **8** was unstable in a

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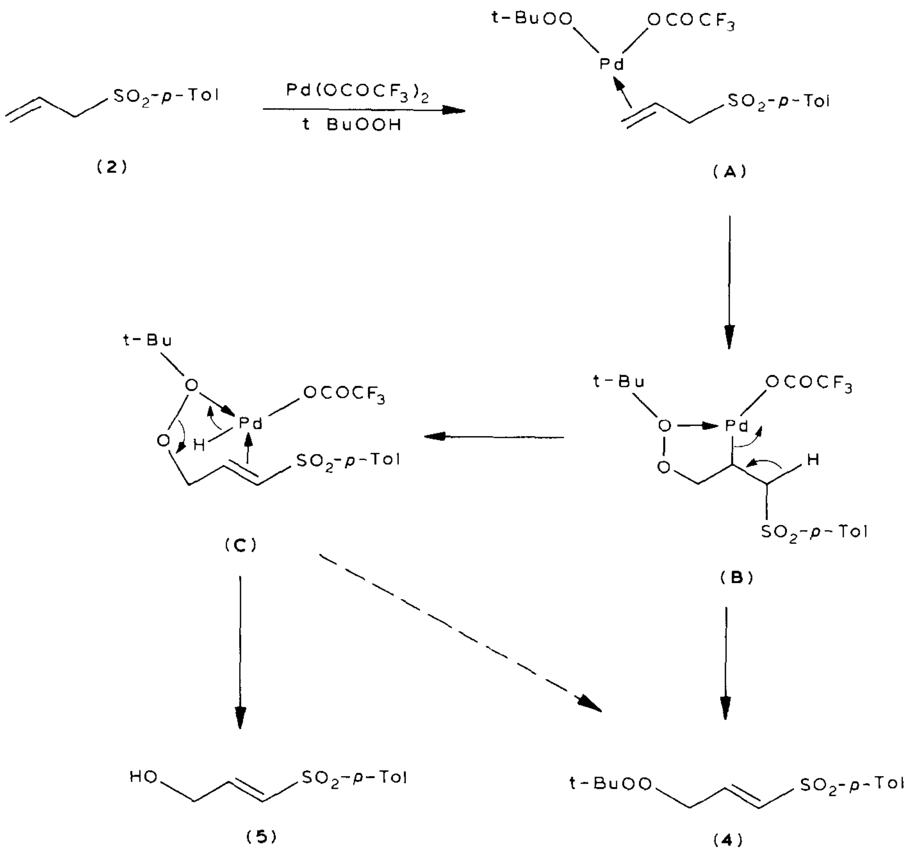
* A referee has pointed out that use of DMF as solvent favours the formation of η^3-allylpalladium complexes. Although this solvent has sometimes been preferred in the preparation of such complexes [22], a mixture of DMF and H_2O is generally used to oxidize terminal alkenes to ketones [6].



Scheme 3

DMSO solution and gave the alcohol **5** [18]. This alcohol could be oxidized into **1** under the reaction conditions of the Table 2. Meanwhile, it appears that higher yields (yield = conversion × selectivity) in **1** + **5** are obtained from **3** (runs 7–9) than **2** (runs 4–6). Thus, the desilylated alkene **2** can be involved only in part during oxidation of **3**. A more efficient formation of the η^3-allylpalladium derivative **8** from **3** rather than **2** [5] could account for these results.

Experimental

The preparations and characteristics of **1**, **2**, **5** and the metal salts have been described previously (see ref. 4 and references therein). Alcohol **2** can also be obtained from epichlorhydrin and sodium *p*-toluenesulphinate under phase transfer conditions [19]. Complexes **7** and **8** were obtained by Trost's procedure [20]; the instability of **7** precluded its isolation; **8** has been described previously [18]. Anhydrous toluene solutions of t-BuOOH were obtained by Sharpless's procedure [21]. A rubber balloon filled with O_2 was used for reactions carried out in the presence of oxygen. Work-up procedures were similar to that previously described [4], and separation of the products were carried out on silica TLC plates.

1-(Trimethylsilyl)-1-(p-toluenesulfonyl)-2-propene (3)

A solution of **2** in THF was added dropwise to a solution of n-butyllithium (1.1 equiv.) in hexane at −78 °C. After 15 min, trimethylsilylchloride (1.3 equiv.) was added. Stirring was maintained for 1 h then the cold bath was removed and brine was added in one portion. Extraction was performed with ether. The organic phase was dried over sodium sulfate and evaporated under reduced pressure to leave oil, which was crystallised from a methylene chloride/petroleum ether mixture.

Yield: 96%; m.p. 82–84 °C; IR ($CHCl_3$): 1315, 1302, 1290, 1253, 1140, 1085, 920, 850 cm^{-1}; ^1H NMR ($CDCl_3$): 2.13 (3H, s); 3.19 (1H, d, *J* 10 Hz); 4.3–4.9 (2H, m); 5.4–5.9 (1H, m); 6.96 (2H, d, *J* 8 Hz); 7.40 ppm (2H, d, *J* 8 Hz); Microanalysis: Found: C, 58.25; H, 7.44. $C_{13}H_{20}SO_2Si$ calcd.: C, 58.14; H, 7.51%.

Oxidation by t-BuOOH / Pd(OCOCF$_3$)$_2$

An anhydrous t-BuOOH solution in toluene (3.1 *M*; 6.5 ml) was added to a mixture of **2** (or **3**) (5 mmol) and $Pd(OCOCF_3)$ (116 mg, 0.35 mmol) in toluene (20 ml). The mixture was stirred at 50 °C for 3 days and then worked up in the usual way.

3-(t-Butylperoxy)-1-(p-toluenesulphonyl)-1-propene (4)

Oil; IR ($CHCl_3$): 1318, 1302, 1145, 1085 cm^{-1}; ^1H NMR ($CDCl_3$): 1.2 (9H, s), 2.42 (3H, s), 4.60 (2H, d.d., *J* 1.5 and 4 Hz), 6.54 (1H, dt, *J* 15 and 1.5 Hz), 6.96 (1H, d.t., *J* 15 and 14 Hz), 7.32 (2H, d, *J* 8 Hz), 7.77 ppm (2H, *J* 8 Hz); Microanalysis: Found: C, 59.05; H, 7.03. $C_{14}H_{20}SO_4$ calcd.: C, 59.13; H, 7.09%.

3-(t-Butyloxy)-1-(p-toluenesulphonyl)-1-propene (6)

Isobutene was bubbled for 10 min into a stirred solution of alcohol **5** in methylene chloride at −40 °C. The mixture was left overnight. Conventional work-up gave the ether **6**. Yield: 55%; IR ($CHCl_3$): 1312, 1300, 1278, 1188, 1142, 1118, 1085 cm^{-1}; ^1H NMR ($CDCl_3$): 1.17 (9H, s), 2.42 (3H, s), 4.10 (2H, dd, *J* 3 and 2 Hz), 6.58 (1H, dt, *J* 15 and 2 Hz), 6.98 (1H, dt, *J* 15 and 3 Hz), 7.30 (2H, d, *J* 8 Hz), 7.75 ppm (2H, d, *J* 8 Hz).

Reduction of 4

A suspension of **4** (17 mg) and potassium iodide (15 mg) in benzene (5 ml) containing acetic acid (1 ml) was heated under reflux for 5 h under argon. Conventional work-up gave the alcohol **5** (5 mg), which was shown to be identical with an authentic sample (T.L.C., IR and NMR).

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