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Anaerobic Palladium-Catalyzed Chemoselective Oxidation of Allylic and Benzylic Alcohols with α-Bromo Sulfoxide as a Co-oxidant

Nuria Rodríguez,[a] Mercedes Medio-Simón,[a] and Gregorio Asensio[a,]*

[a] Departamento de Química Orgánica, Universidad de Valencia, Avenida Vicent Andrés Estellés s/n, 46100 Burjassot, Valencia, Spain
Fax: (+34)-96-354-4939; e-mail: gregorio.asensio@uv.es

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Dedicated to Prof. M. Yus on the occasion of his 60th birthday.

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Abstract: A chemoselective palladium-catalyzed anaerobic oxidation of allylic and benzylic alcohols using an α-bromo sulfoxide as a co-oxidant is described for the first time. The catalyst system is simple and has a long life because of the allowance of phosphane ligands under the non-aerobic conditions. The advantages of the described method include no overoxidation of primary alcohols to carboxylic acids because of the mild conditions applied, the tolerance of oxygen-sensitive functionalities such as a carbon-carbon double bond, an organothio group, or a diorganoamino group and the effective preparation of α,β-unsaturated aldehydes and ketones, resulting from the oxidation of primary and secondary allylic alcohols, since a competitive Heck reaction with the co-oxidant does not occur.

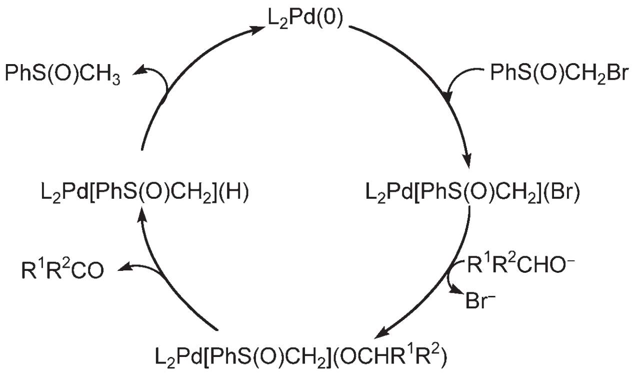
Keywords: alcohols; homogeneous catalysis; oxidation; palladium; sulfur

Introduction

The oxidation of alcohols to aldehydes and ketones is one of the most important functional group transformations in organic synthesis.[1] Although many reagents are available to accomplish this key reaction, most of them are required in stoichiometric quantities and are either toxic, hazardous or both. To circumvent these problems, catalytic oxidation processes based on the combination of a salt of a metal such as V, Mo, Ru, Co, Cu, Ni or Pd and stoichiometric oxidants have been devised.[2] In this context, the development of procedures that use molecular oxygen as the sole re-oxidant has been extensively pursued for economic and ecological reasons.[3,4] However, there are some persistent problems: a) the stability of metal ligands under aerobic oxidation conditions and b) metal aggregation and precipitation, which cause catalyst decomposition with a considerable loss of catalytic activity that occurs mainly under ligand-free conditions. This problem is particularly important in the case of Pd. So, although Pd is perhaps one of the most active and versatile transition metals, it has received comparatively little attention in oxidation chemistry, probably because phosphanes, which are standard palladium ligands, are incompatible with aerobic oxidation conditions. Nitrogen ligands have been used with relative success, but the reaction conditions must be properly fixed to avoid the easy formation of Pd black. These key conditions are: a sufficient oxygen partial pressure (typically 1 atm molecular oxygen) and a low molar ratio of substrate to catalyst (S/C: typically 20 or less). To circumvent these limitations, recent effort has been focused on the preparation of dendrimers as palladium ligands.[5] Another important point that is associated with the difficulty of aerobic oxidation is the restrictions in the type of alcohol that can be oxidized. In fact, alcohols with oxygen-sensitive functionalities such as C=C, $-SR$ and $-NR_2$ are not suitable substrates. An alternative to the aerobic homogeneous transition metal oxidation of alcohols is the anaerobic version.[6] In this alternative, re-oxidation of the transition metal is generally based on a non-O-containing compound. Halogen-based co-oxidants have been used for this purpose. This approach based in the oxidation of Pd(0) by halogenated compounds has been applied not only in the oxidation of alcohols but also in other process such as the homocoupling of alkynes[7] and boronic acids[8] to give diynes and symmetrical biaryls, respectively. Regarding the oxidation of alcohols, bromobenzene was used as an effective co-oxidant in the Pd-catalyzed transformation of secondary aliphatic and benzylic alcohols in the corresponding carbonyl derivatives.[9] However, the application of this protocol to secondary α,β-unsaturated alcohols was often disappointing, since in this case a competitive Heck reaction took place. Substitution of bromobenzene by the more sterically-hindered halide 2-bromomesitylene retards the Heck reaction, and allows a much more selective oxidation procedure. The reaction requires a basic medium and the type of base is an important factor. Soft bases are preferred because aldol condensation of the reaction product is precluded. Palladium-catalyzed oxidations based on chlorohydrocarbons that were used both as a solvent and a co-oxidant have also been described.[10] With carbon tetrachloride, secondary aliphatic and benzylic alcohols were efficiently oxidized but allylic alcohols with a double bond in a terminal position did not give the corresponding α,β-unsaturated ketones because CCl_4 readily underwent Pd-catalyzed addition to the double bond. With 1,2-dichloroethane[11] as a co-oxidant, problems were encountered in the oxidation of primary alcohols, which gave mixtures of aldehydes and esters (overoxidation), and with allylic alcohols because of competing migration of the double bond. Recently, chloroarenes[12] have been described as co-oxidants but the procedure requires special ligands. Despite the diverse methods that have been previously described for the palladium-catalyzed oxidation of alcohols to aldehydes and ketones using aerobic and anaerobic conditions, the development of more selective procedures that allow for the oxidation of primary alcohols to aldehydes without overoxidation is needed; the efficient discrimination of diverse functional groups as well as oxygen-sensitive functionalities and the suppression of competitive reactions remain challenging.

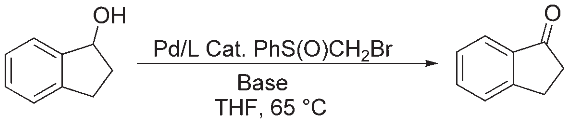
Results and Discussion

We report here our approach to the non-aerobic palladium-catalyzed oxidation of alcohols using an α-bromo sulfoxide as a co-oxidant. The procedure is based on the hydrodebromination of the α-bromo sulfoxide which takes place when the palladium cross-coupling reaction[13] is tried with alcohols. In this case, an inefficiency in the formation of C–O bonds occurs because of competing β-hydrogen elimination from the complex $Ln_2Pd[PhS(O)CH_2](OR)$. Subsequent reductive elimination leads to the hydrodebromination product ($PhSOCH_3$) (Scheme 1).



Scheme 1. Catalytic cycle for oxidation of alcohols with α-bromo sulfoxide as co-oxidant.

First, we tested if the uncatalyzed reaction between α-bromomethyl phenyl sulfoxide and alkoxides took place. Although the nucleophilic substitution reaction of α-bromomethyl sulfoxides with alkoxides in alcohol as a solvent has been described,[14] we proved that this reaction does not occur in an aprotic solvent (THF).[15] Next, we performed two control experiments to unequivocally prove that the α-bromo sulfoxide acts as a co-oxidant in the palladium-catalyzed oxidation of alcohols. Runs were performed using 1-indanol as a substrate and $Pd(PPh_3)_4$ as a catalyst [Eq. (1)].



(1)

Initially, the α-bromo sulfoxide was omitted from the reaction medium. Under these conditions, the 1-indanol was recovered unchanged. A second control experiment was performed to test the eventual participation of the sulfinyl group in the oxidative catalytic cycle. When the α-bromo sulfoxide was substituted by methyl phenyl sulfoxide, the 1-indanol was recovered unaffected. Thus, both experiments showed that the catalytic cycle occurs only in the presence of the α-bromo sulfoxide. Subsequently, we performed various reactions to determine the appropriate reaction conditions with regard to the type of base and the type of phosphane ligand. Again, 1-indanol was used as a prototype substrate in these runs [Eq. (1), Table 1]. Among the bases tested, K_3PO_4 was the most suitable (Table 1, entries 1–5). The amount of base was also optimized. Better yields were found by using 4 equivs. of K_3PO_4 (Table 1, entries 1 and 6–9). The degree of conversion in the oxidation reaction was largely dependent on the palladium ligand. The catalyst generated from $Pd(OAc)_2$ and the bidentate phosphane BINAP proved to be more active in the oxidation reaction, (Table 1, entry 8) in agreement with the reported good hydride acceptor character of palladium complexes of diphosphanes with a large bite angle.[16] So, the bidentate phosphane di-PHOS, with a smaller

Table 1. Palladium-catalyzed oxidation of 1-indanol with α-bromo sulfoxide as co-oxidant varying the bases and the catalyst.

Entry	Base (equivs.)	Catalyst (mol %)	Yield [%]
1	K_3PO_4 (4)	$Pd(PPh_3)_2Cl_2$[a]	78
2	Cs_2CO_3 (4)	$Pd(PPh_3)_2Cl_2$[a]	66
3	K_2CO_3 (4)	$Pd(PPh_3)_2Cl_2$[a]	50
4	$Ba(OH)_2$ (4)	$Pd(PPh_3)_2Cl_2$[a]	47
5	Na_2CO_3 (4)	$Pd(PPh_3)_2Cl_2$[a]	18
6	K_3PO_4 (3)	$Pd(PPh_3)_2Cl_2$[a]	66
7	K_3PO_4 (2)	$Pd(PPh_3)_2Cl_2$[a]	51
8	K_3PO_4 (4)	$Pd(OAc)_2$[a]/BINAP[b]	89
9	K_3PO_4 (2)	$Pd(OAc)_2$[a]/BINAP[b]	56
10	K_3PO_4 (4)	$Pd(OAc)_2$[a]/BINAP[c]	47
11	K_3PO_4 (4)	$Pd(OAc)_2$[a]/diPHOS[b]	37
12	K_3PO_4 (4)	$Pd(OAc)_2$[a]/PPh_3[c]	45
13	K_3PO_4 (4)	$Pd(OAc)_2$[a]/PPh_3[d]	33
14	K_3PO_4 (4)	$Pd(OAc)_2$[a]/P(*o*-tolyl)$_3$[c]	33
15	K_3PO_4 (4)	$Pd(OAc)_2$[a]/P(cyclohexyl)$_3$[c]	52
16	K_3PO_4 (4)	$Pd(OAc)_2$[a]/P(*p*-anisyl)$_3$[c]	47

[a] 10 mol%.

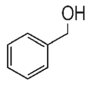
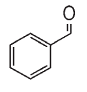
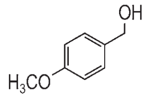
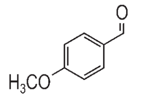
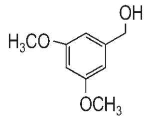
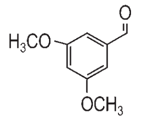
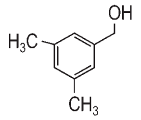
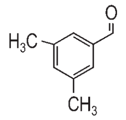
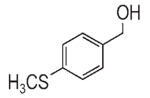
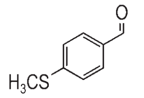
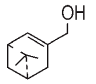
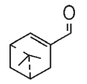
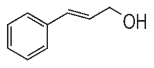
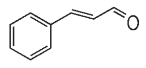
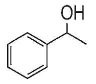
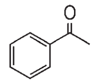
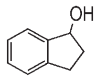
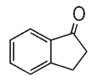
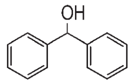
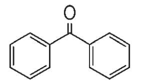
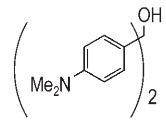
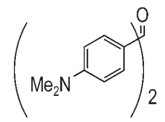
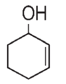
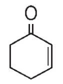
[b] Ratio 1:1.

[c] Ratio 1:2.

[d] Ratio 1:4

bite angle, was significantly less effective (Table 1, entry 11). On the other hand, the catalytic system formed by $Pd(OAc)_2$ and monodentate phosphanes such as the PPh_3 (Table 1, entry 12), the electron-rich P(*o*-tolyl)$_3$ (Table 1, entry 14) and P(*p*-anisyl)$_3$ (Table 1, entry 16) or the electron-rich and sterically hindered PCy_3 (Table 1, entry 15), led also to poor results. For a given phosphane, differences were found depending on the palladium source (Table 1, entries 1 and 12). This fact can be related to the better coordinating ability of acetate to the metal, disfavouring the creation of vacancies in the palladium sphere that are essential for the progress of the reaction. Moreover, the influence of halides in the oxidative addition step should play a role.[17] The optimal ratio of phosphane to palladium was also tested. The rates of oxidation were greater when a 1:1 ratio of bidentate phosphane to palladium (Table 1, entries 8 and 10) and a 2:1 ratio of monodentate phosphane to palladium were used (Table 1, entries 12 and 13). Once we determined the optimal conditions for the reaction, we tested the substrate scope of this new palladium-catalyzed oxidation. Primary and secondary allylic and benzylic alcohols that were either unsubstituted or contained electron-donating groups at the benzene ring reacted efficiently to afford the corresponding carbonyl compounds in moderate to high isolated yields (Table 2). Notably, no overoxidation of primary alcohols to carboxylic acids was observed (Table 2, entries 1–7)[18], oxygen-sensitive functionalities such as C=C, −SR, $-NR_2$ remained unaffected under these oxygen-free reactions (Table 2, entries 5 and 11) and α,β-unsaturated aldehydes and ketones resulting from the oxidation of primary and secondary alcohols did not undergo competitive Heck reactions with the co-oxidant (Table 2, entries 6, 7 and 12). Benzylic alcohols containing electron-withdrawing groups or chelating groups next to the hydroxy group and aliphatic primary and secondary alcohols did not react under

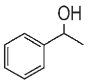
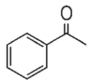
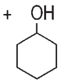
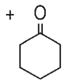
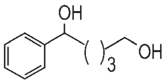
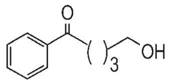
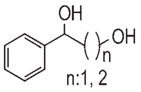
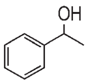
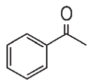
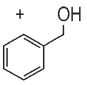
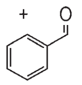
Table 2. $Pd(OAc)_2$/BINAP-catalyzed oxidation of allylic and benzylic alcohols in basic medium (K_3PO_4).[a]

Entry	Alcohol	Product	Yield [%]
1			40
2			78
3			91
4			55
5			81
6			82
7			99
8			99
9			80
10			98
11			98
12			98

[a] The reactions were performed in THF at 65 °C. Molar equivalents of the reagents and catalyst were as follows: ROH (1.0 mmol), $PhS(O)CH_2Br$ (1.0 mmol), K_3PO_4 (4.0 mmol), $Pd(OAc)_2$ (10% mmol), BINAP (10% mmol). Reaction time 12 h. Yields correspond to isolated product

our standard conditions. One exception among the saturated alcohols was 2-phenylcyclohexanol which underwent reaction although sluggish. The slight activation can be related with the presence of an unsaturated bond close to the hydroxy group since similar aliphatic alcohols, without the unsaturated bonds or with the hydroxy group far away from the unsaturation, such cyclohexanol and 3-phenylcyclohexanol were unreactive. High inter- and intramolecular chemoselectivity was found in the oxidation of benzylic versus aliphatic alcohols (Table 3). Indeed, the reaction of a 1:1 mixture of alcohols resulted in complete transformation of the benzylic alcohol whereas aliphatic alcohols remained unchanged (Table 3 entry 1). A similar degree of selectivity was found in the oxidation of the 1,5-diol: after the reaction was complete, only the benzylic moiety was oxidized (Table 3, entry 2). However, the catalyst does not tolerate the presence of strongly coordinating groups closer to the hydroxy groups and oxidation was completely inhibited for 1,2- or 1,3-diols. (Table 3, entry 3). On the other hand, only slight selectivity was observed in the competitive oxidation of primary and secondary benzylic alcohols (Table 3, entry 4).

Table 3. Inter-and intramolecular selectivity in the palladium catalyzed oxidation with α-bromo sulfoxide as co-oxidant.

Entry	Alcohols	Products	Yield [%]
1			92
			<1
2			98
3		NR	0
4			60
			40

Conclusions

In summary, our methodology constitutes a new and highly chemoselective procedure for the oxidation of allylic and benzylic alcohols. The anaerobic method allows the use of phosphanes that give a long life to the catalyst since its precipitation as palladium black is retarded. In addition oxygen-sensitive functionalities such as C=C, $-$SR, $-$NR$_2$ remained unaffected under these oxygen-free reactions and the mild reaction conditions do not allow overoxidation of primary alcohols to carboxylic acids. Remarkably, allylic alcohols that are poor substrates in the aerobic palladium-catalyzed oxidation are oxidized in excellent yields by our procedure. The lack of reactivity of the resulting α,β-unsaturated aldehydes and ketones in Heck reactions with the co-oxidant may be the key to the particular efficiency of our method in the oxidation of allylic alcohols. Although many catalytic air oxidations proceed more rapidly with allylic and benzylic substrates, the essentially complete chemoselectivity observed here is not common. The standard reagent currently used for the selective oxidation of allylic and benzylic alcohols is manganese dioxide. While MnO$_2$ shows excellent chemoselectivity, its use is associated with problems such as the need for overstoichiometric amounts of the oxidant, which results in the generation of substantial quantities of inorganic waste. In our procedure, palladium is used in a relatively low loading and the co-oxidant, the α-bromo sulfoxide, can be reused by simple bromination of the sulfoxide resulting from its reduction in the catalytic cycle. In addition, the sulfoxide can be easily separated in the work-up from the aldehydes or ketones obtained in the reaction.

Experimental Section

General Methods

Proton magnetic resonance and carbon magnetic resonance spectra were recorded at 300 MHz and 75 Hz, respectively. Chemical shifts are reported in δ ppm relative to the CHCl$_3$ peak at 7.27 ppm (^{1}H) or 77.0 ppm (^{13}C). GC analysis was performed with an Agilent HP-5 ms ($30\ \mathrm{m}\times 250\ \mu\mathrm{m}\times 0.25\ \mu\mathrm{m}$) capillary column. Reactions were monitored by analytical thin layer chromatography using commercial aluminium sheets pre-coated (0.2 mm layer thickness) with silica gel 60 F$_{254}$. Product purification by flash chromatography was performed using silica gel (230–400 mesh).

Materials

Tetrakis(triphenylphosphine)palladium and Pd(OAc)$_2$ were purchased from Johnson Matthey. 1-Phenyl-1,5-pentanediol (Table 3, entry 2) was prepared in two steps from commercial 4-benzoylbutyric acid following reported procedures.[19,20]

The commercial carbonyl compounds obtained were identified by ^{1}H NMR and their purity was ascertained by GC analysis of the 1:1 mixture with an authentic pure sample giving a single peak in all the cases. (**I-230–4** 1-indanone; **B133–4** benzaldehyde; **A8,810–7** *p*-anisaldehyde; **12,629–3** 3,5-dimethoxybenzaldehyde; **51,805–0** 3,5-dimethylbenzaldehyde; **22,277–1** 4-(methylthio)benzaldehyde; **21,824–3** (1*R*)-(−)-myrtenal; **23,996–8** *trans*-cinnamaldehyde; **A1,070–1** acetophenone; **42,755–1** benzophenone; **14,783–4** 4,4′-bis(dimethylamino)benzophenone; **C10,281–4** 2-cyclohexen-1-one). GC analysis was performed with an Agilent HP-5 ms (30 m × 250 μm × 0.25 μm) capillary column heated gradually to 340 °C (from 70 °C, rate 15 °C min^{-1}). Vector gas: He$_2$. Column head pressure: 7.69 psi.

Preparation of Bromomethyl Phenyl Sulfoxide[21]

To a solution of methyl phenyl sulfoxide (10 mmol) and anhydrous pyridine (22 mmol) in dry acetonitrile (40 mL) cooled at −40 °C under an argon atmosphere was added dropwise a solution of bromine (20 mmol) in dry acetonitrile (20 mL) at −20 °C. The mixture was stirred first at −40 °C for 1 h and then overnight at room temperature. The solvent was evacuated in vacuum and the residue was redissolved in dichloromethane. The organic layer was washed with Na$_2$S$_2$O$_3$ (0.02 N, 30 mL), dried over anhydrous Na$_2$SO$_4$ and concentrated to dryness. The crude material was purified by flash column chromatography (hexane:ethyl acetate 5:1) to afford the sulfoxide; yield: 80 %.^{1}H NMR (·300 MHz, CDCl$_3$): $\delta = 4.16$–4.30 (AB, $J = 12.3$ Hz, 2 H), 7.50–7.47 (m, 2 H) 7.61–7.64 (m, 3 H); ^{13}C NMR (·75 MHz, CDCl$_3$): $\delta =$ 48.8 (t), 124.7 (d), 129.2 (d), 132.0 (d), 141.5 (s); HR-MS (EI): $m/z = 217.9363$, calcd. for C$_7$H$_7$BrOS (M$^+$): 217.9401.

1-Phenylpentane-1,5-diol (Table 3, entry 2): ^{1}H NMR (·300 MHz, CDCl$_3$): $\delta = 1.80$–1.20 (m, 6 H), 3.56 (t, $J =$ 5.30 Hz, 2 H), 4.61 (dd, $J = 7.50$ and 5.60 Hz, 1 H), 7.30–7.20 (m, 5 H);. ^{13}C NMR (·75 MHz, CDCl$_3$): $\delta = 22.0$(t), 32.4(t), 38.7(t), 62.7(t), 74.5(d), 125.8(d), 127.5(d), 128.4(d), 144.7(s); HR-MS (EI): $m/z = 180.1157$, calcd. for C$_{11}$H$_{16}$O$_2$ (M$^+$): 180.1150.

5-Hydroxy-1-phenylpentan-1-one (Table 3, entry 2): ^{1}H NMR (·300 MHz, CDCl$_3$): $\delta = 1.80$–1.20 (m, 4 H), 3.00–2.90 (m, 2 H), 3.70–3.55 (m, 2 H), 7.45–7.35 (m, 3 H), 7.90–7.80 (m, 2 H); ^{13}C NMR (·75 MHz, CDCl$_3$): $\delta = 20.1$(t), 32.2(t), 38.1(t), 62.3(t), 128.0(d), 128.5(d), 133.0(d), 136.9(s), 200.4(s); HR-MS (EI): $m/z = 178.0994$, calcd. for C$_{11}$H$_{14}$O$_2$ (M$^+$): 178.0995.

Palladium-Catalyzed Anaerobic Oxidation of Alcohols; General Procedure

A mixture of the appropriate alcohol (0.4 mmol), K$_3$PO$_4$ (339.6 mg, 1.6 mmol), Pd(OAc)$_2$ (8.9 mg. 0.04 mmol) and racemic BINAP (12.4 mg, 0.02 mmol) was loaded in a Schlenk reaction tube. The mixture was degassed by alternative vacuum and argon purge cycles. α-Bromo sulfoxide (86.8 mg, 0.4 mmol) and THF (4 mL) were added and the mixture was heated at 65 °C for 12 h. The reaction mixture was taken up in ether (20 mL) and washed with a saturated NH$_4$Cl aqueous solution and brine. The organic phase was dried over MgSO$_4$, filtered, and concentrated under vacuum. The crude product was purified by column chromatography on silica gel to afford the corresponding carbonyl compound.

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