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Palladium-Catalyzed Aerobic Oxidation of Naturally Occurring Allylbenzenes as a Route to Valuable Fragrance and Pharmaceutical Compounds

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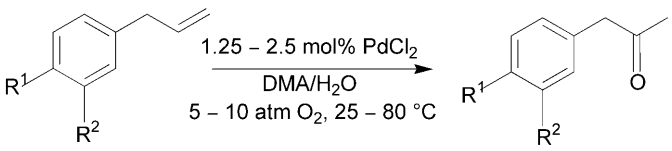
Abstract: A palladium-catalyzed, aerobic oxidation of naturally occurring allylbenzenes, i.e., eugenol, methyleugenol, safrole, and estragole, in dimethylacetamide/water solutions under mild conditions has been developed, in which palladium(II) chloride is used in the absence of co-catalysts or special stabilizing ligands as the sole and recyclable catalyst. Methyl ketones that are important for the flavour and pharmaceutical industries have been obtained in good to excellent yields with low catalyst loadings (1–2 mol%) and high average turnover frequencies. This simple catalytic method represents an ecologically benign and economically attractive route to industrially valuable compounds starting from renewable substrates easily available from essential oils.

Keywords: allylbenzenes; methyl ketones; oxidation; oxygen; palladium

Introduction

The functionalization of naturally occurring olefins can provide oxygenated compounds that are valuable in the fine chemicals industry. We have recently reported that various fragrance alcohols, ketones, aldehydes, and esters can be obtained in good yields by the metal complex-catalyzed oxidation[1,2] and hydroformylation[3–5] of natural terpenic olefins. Substituted allylbenzenes that are easily available from biomass, such as eugenol (**1a**), methyleugenol (**2a**), safrole (**3a**), and estragole (**4a**) (Scheme 1), are also an important renewable feedstock for flavour and fragrance industries; in addition, their oxygenated derivatives often show biological and phytosanitary activities and are useful in the pharmaceutical industry.[6]



	Compound	R^1	R^2	
1a	eugenol	OH	OCH_3	**1b**
2a	methyleugenol	OCH_3	OCH_3	**2b**
3a	safrole	-O-CH_2-O-		**3b**
4a	estragole	OCH_3	H	**4b**

Scheme 1. Oxidation of allylbenzenes into methyl ketones.

Palladium-catalyzed selective oxidations represent a versatile method to introduce an oxygen-containing functionality into organic molecules. These reactions are especially attractive when molecular oxygen is involved as a final oxidant, which is usually achieved by using $CuCl_2$ as co-catalyst to re-oxidize reduced palladium species (Wacker catalyst).[7] However, the Wacker process requires large amounts of chloride ions and acid to maintain a catalytic cycle; therefore, the system is highly corrosive and often causes the formation of chlorinated side products. Although systems with various alternative halide-free co-catalysts, such as $Cu(OAc)_2$, heteropoly acids, nitrates, and benzoquinone, have been intensively studied in attempts to reduce the environmental impact of these processes,[8–14] the reoxidation of palladium(0) during the catalytic cycle under more friendly conditions remains a critical challenge.

Important recent advances in this field consist in the use of oxidatively robust ligands to stabilize reduced palladium and promote its regeneration directly by molecular oxygen avoiding the use of corrosive and waste-generating additives.[14–20] Nevertheless, only a few examples of ligand-modulated palladium-catalyzed oxidations of terminal alkenes into methyl

ketones using molecular oxygen as the sole oxidant have been published.[15,16,20] Recently, Kaneda and coworkers have discovered that the use of dimethylacetamide as a solvent allows one to perform an aerobic oxidation of a number of terminal alkenes without the need for additional co-catalysts or special ligands.[21] In this system, the solvent seems to stabilize a palladium catalyst preventing its precipitation into inactive metal.

Inspired by these disclosures and in the context of our program aimed at adding value to natural ingredients of renewable essential oils, we decided to study the oxidation of naturally occurring substituted allylbenzenes **1a**–**4a**. Although palladium-catalyzed oxidations of these alkenes are expected to give phenyl-2-propanones, which are widely used as intermediates in pharmaceutical synthesis and particularly important for the production of antihypertensive α-methyldopa,[23,24] the data published on this subject are really scarce.[25–27] A probable reason for this is the reported anomalous behaviour of eugenol and estragole in the conventional $PdCl_2/CuCl_2$ Wacker system, as the reaction does not lead to expected carbonyl compounds but rather gives dimeric and/or oxidative cleavage products.[26] A corresponding methyl ketone was obtained from safrole in *ca.* 50% yield only by using *p*-benzoquinone (BQ) as a stoichuiometric oxidant in methanol solutions with catalytic amounts of $PdCl_2$.[27]

In the present paper, we report a simple and efficient palladium-catalyzed direct-dioxygen-coupled oxidation of eugenol, methyleugenol, safrole, and estragole which gives valuable methyl ketones in good to excellent yields. The reactions do not need additional co-oxidants or special ligands and proceed under mild aerobic conditions. The use of $PdCl_2$ as the sole catalyst and inexpensive high boiling amidic solvents as well as molecular oxygen as the final oxidant are significant practical advantages of the process. All obtained products have a pleasant scent with flower or fruit tinge and could be useful as components of synthetic perfumes in addition to their applications in pharmaceutical industry.

Results and Discussion

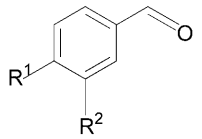
For several years, our research group has been interested in the palladium-catalyzed aerobic oxidations of naturally occurring olefins.[12,14,28] Studying the reactivity of eugenol and safrole we observed that their acetic acid solutions with catalytic amounts of $PdCl_2$, $CuCl_2$, and LiCl readily consumed dioxygen; however, only small amounts of the corresponding methyl ketones were detected. Most of the reacted substrates were converted into high boiling products which were not detectable by GC. Trying to clarify these observations, we ran the reaction with eugenol in the absence of palladium and found that the solution still consumed dioxygen. As a result of that study, we have discovered the novel process of nuclear oxychlorination of phenolic compounds and, then, aromatic amines catalyzed by $CuCl_2$.[29,30] On the other hand, the problem with the selective oxidation of olefinic bonds in the molecules of eugenol and safrole remained unsolved.

Our various attempts to oxidize eugenol in the conventional palladium-based systems, such as $Pd(OAc)_2/LiNO_3/O_2$, $Pd(OAc)_2$/BQ, $Pd(OAc)_2$/BQ/$Cu(OAc)_2/O_2$, gave no promising results due to a great difference in the reaction mass balance; in other words, eugenol underwent unselective transformations with the predominant formation of the products which were not detectable by GC. Encouraged by recent advancements in palladium-catalyzed aerobic oxidations,[17] we have decided to work with these problematic substrates using molecular oxygen as the sole oxidant.

The oxidations of eugenol (**1a**), methyleugenol (**2a**), safrole (**3a**), and estragole (**4a**) with dioxygen were studied in dimethylacetamide (DMA) or dimethylformamide (DMF) solutions containing 1–2 mol% of $PdCl_2$ and 15–20 vol% of water. In most of the runs, elevated pressures of oxygen were used in order to ensure efficient capture of the reduced palladium and prevent metal precipitation. Some experiments were performed at atmospheric pressure. The reactions with each substrate resulted in corresponding methyl ketones **1b**–**4b** (Scheme 1) as major products, which were obtained in 70–90% yields in most of the runs. A GC mass balance was based on the substrate charged using bornyl acetate as an internal standard. The difference in the mass balance in the runs presented in Table 1 and Table 2 was usually less than 5%. It was attributed to unidentified high boiling products. Thus, a high stability of these delicate substrates toward oligomerization under the conditions used for their oxidation is especially noteworthy taking into account the problems with the mass balance found in the conventional palladium systems.

Minor products of these reactions were vanillin (**1c**), methylvanillin (**2c**), piperonal (**3c**), and *p*-anisaldehyde (**4c**) (Scheme 2) probably formed due to the isomerization of allyl benzenes **1a**–**4a** into the corresponding propenylbenzenes followed by the oxidative cleavage of their olefinic bonds. The cleavage reactions seem to occur through a radical auto-oxidation mechanism. At least, in the related palladium-catalyzed oxidation of styrene, the formation of benzaldehyde was found to be suppressed by adding radical inhibitors to the system.[31] Aldehydes **1c**–**4c** are also useful compounds important for flavour and/or pharmaceutical industries.

We chose eugenol **1a** as a standard substrate to find optimal conditions for the reaction. Eugenol was found to react readily with $PdCl_2$ in DMA solutions



Compound		R^1	R^2
1c	vanillin	OH	OCH_3
2c	methylvanillin	OCH_3	OCH_3
3c	piperonal	-O-CH_2-O-	
4c	*p*-anisaldehyde	OCH_3	H

Scheme 2. Minor products of the oxidation of allylbenzenes **1a**–**4a**.

in the presence of water. A virtually complete conversion has been attained after 6 h at 60 °C and 10 atm resulting in an 84% yield of methyl ketone **1b** and 16% yield of aldehyde **1c** (vanillin) (Table 1, run 1). The reaction is catalytic in palladium and shows a dioxygen-coupled turnover number (TON) of 80, with no palladium mirror being observed on the walls of the autoclave after the reaction. Thus, DMA as a coordinating solvent successfully prevents zerovalent palladium species from clustering into inactive bulk metal and their re-oxidation by molecular oxygen occurs faster than aggregation.

At higher water concentration (20 *vs.* 15 vol%), the reaction is significantly faster and can be completed under these conditions for 4 h showing an almost doubled initial rate and average turnover frequency (TOF) of 17.8 h^{-1} (Table 1, run 2). This value is considerably higher that those usually reported for conventional Wacker oxidations using co-catalysts.[21] The enhancing effect of water was also observed in the Pd/(−)-sparteine/DMA system for the oxidation of other terminal alkenes[20] and in our previous work with styrene.[32] However, a further increase in the water concentration cannot be recommended due to the appearance of problems with the miscibility of the substrate. The relative amounts of ketone **1b** are increased with the water content increase at the expense of vanillin, with the combined yield of these two fragrance compounds remaining almost quantitative.

The kinetic data show that the reaction is roughly first order in palladium, as a 2-fold increase in the concentration of the catalyst leads to a 2-fold increase in the reaction rate (Table 1, run 2 *vs.* run 3 and run 4 *vs.* run 5). On the other hand, the initial reaction rate depends also on the oxygen pressure showing a positive order (Table 1, runs 6 and 7). At 5 atm, no palladium mirror has been observed and the reaction has been completed with only 2.5 mol% of palladium. These observations suggest that the step which determines the rate of the whole process can be the re-oxidation of the reduced palladium species by molecular

Table 1. Palladium-catalyzed oxidation of eugenol **1a** by molecular oxygen.[a]

Run	[Eugenol] [M]	Temperature [°C]	Pressure [atm]	Time [h]	Conversion [%]	Rate[b] [10^{-2} M·h^{-1}]	TON[c]	Selectivity [%] Ketone **1b**	Aldehyde **1c**
1[d]	0.40	60	10	6	100	8.0	80	84	16
2	0.40	60	10	4	99	15.5	80	90	9
3[e]	0.40	60	10	3	100	32.0	40	90	9
4	0.40	50	10	9	100	10.0	80	91	8
5[e]	0.40	50	10	4	100	20.3	40	92	7
6	0.20	60	10	4	100	6.4	40	90	7
7	0.20	60	5	5	99	4.4	40	94	6
8[f]	0.20	60	1	7	15	0.5	6	90	3
9	0.20	60	1	7	32	1.5	13	93	5
10[e]	0.40	80	10	2	99	64.0	40	80	18
11	0.20	80	10	4	98	10.7	40	86	10
12	0.20	100	10	2	100	20.0	40	83	9
13	0.20	25	10	26	100	2.0	40	95	3
14[g]	0.20	60	10	6	76	5.0	30	84	6
15[h]	0.20	60	10	4	100	6.0	80	89	8

[a] *Conditions:* [eugenol] = 0.20 M; [$PdCl_2$] = 0.005 M; gas phase O_2, 10 atm; solvent DMA/H_2O (20 vol%); conversion and selectivity were determined by GC and based on the consumed eugenol.
[b] Initial rate of the substrate conversion.
[c] TON = moles of the substrate converted/moles of Pd.
[d] Solvent DMA/H_2O (15 vol%).
[e] [$PdCl_2$] = 0.01 M.
[f] [(−)-Sparteine] = 0.01 M.
[g] DMF was used as the solvent.
[h] After run 6, the products were separated by extraction with *n*-heptane, the reactor was recharged with fresh eugenol and the reaction was allowed to proceed further. TON is given for two reaction cycles.

oxygen. On the other hand, the oxygen-dependence can also reflect the competition between the re-oxidation of the Pd(0) intermediates and their aggregation to catalytically inactive palladium black, as it has been observed at the aerobic oxidation of alcohols in related palladium systems.[33–35] Additional kinetic studies are necessary to clarify the mechanism of these reactions. No substantial changes in the product selectivities have been observed with varying pressure and catalyst concentration.

The reaction is also catalytic in palladium at an ambient pressure of oxygen in the presence of (−)-sparteine (1 equivalent to Pd) used to stabilize reduced palladium species[20] (Table 1, run 8). No formation of palladium mirror occurs, but the reaction is slow and becomes stagnated at near 15% conversion (TON = 6). In the absence of the auxiliary ligand, the reaction also occurs at 1 atm of oxygen, with *ca.* 30% of the substrate being gradually converted during 7 h (TON = 13) (Table 1, run 9). However, then the conversion again became stagnated. Thus, an elevated pressure of oxygen, at least 5 atm, must be used to keep the catalytic system active in the oxidation of eugenol.

The reaction can be significantly accelerated by the increase in temperature, being completed within 2 h at 80 °C without loss in the combined yield of methyl ketone and vanillin which remains excellent (Table 1, *cf.* runs 3 and 10). On the other hand, at higher temperature the contribution of the carbon-carbon bond cleagave giving vanillin becomes higher. A treatment of the kinetic data revealed the temperature dependence for this reaction. The data on the reaction rates expressed by means of the Arrhenius equation yield an activation energy of *ca.* 38 kJ·mol^{-1} in the range of 50–80 °C (Table 1, runs 3, 5, and 10; Figure 1). Another set of the runs (Table 1, runs 6, 11–13; Figure 1) collaborates with this value for activation energy and allows us to extend the temperature range to 25–100 °C. At 100 °C, the reaction is very fast but less selective, as the combined yield of two main products decreases to 92% (Table 1, run 12). It is important that the catalytic system efficiently operates at room temperature. Although the reaction expectedly becomes slower, it can be completed with only 2.5 mol% palladium and shows a 95% yield of methyl ketone, which is the highest value obtained in the present work (Table 1, run 13).

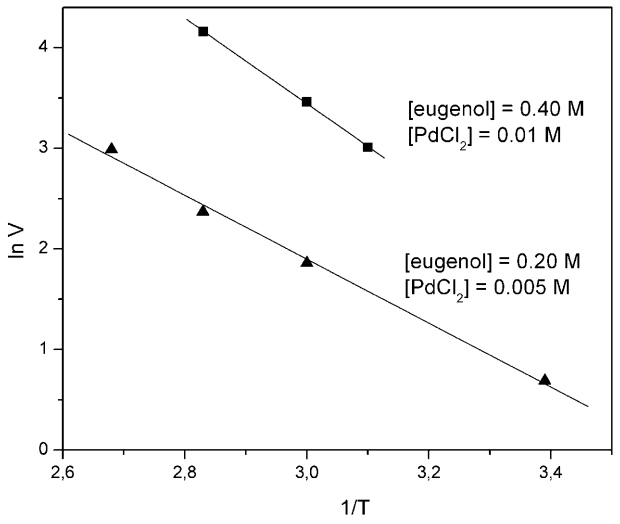


Figure 1. Palladium-catalyzed oxidation of eugenol: temperature effect. *Conditions:* gas phase O_2, 10 atm; solvent DMA/H_2O (20 vol%).

The palladium-catalyzed oxidation of eugenol also shows a dioxygen-coupled TON in another amidic solvent, DMF (Table 1, run 14 *vs.* run 6). It occurs at a slightly lower rate and not with the same efficiency as in DMA becoming stagnated at 75% conversion of the substrate; however, no formation of palladium mirror has been observed. This result is remarkable in the light of a previously reported observation that 1-decene gives only a trace yield of the corresponding methyl ketone in DMF under similar conditions.[21] Thus, DMF also promotes the regeneration of the palladium species at the oxidation of eugenol without the need of co-catalysts or special ligands; however, the reaction stagnation could indicate a partial catalyst decomposition that is not visible by simple visual inspection. Selectivity for methyl ketone in DMF is slightly lower than in DMA (84 *vs.* 90%), but the reaction variables have not been optimized yet.

The DMA solution of $PdCl_2$, in principle, can be re-used without any treatment after the separation of the oxygenated products by extraction with *n*-heptane upon completion of the reaction. The residual solution after run 6 was recharged with fresh eugenol and stirred under identical conditions. The reaction rate with the recharged substrate varied only slightly and the selectivity for methyl ketone **1b** was 89% (Table 1, run 15).

Other naturally occurring allylbenzenes, i.e., methyleugenol, safrole, and estragole, can also be oxidized smoothly by molecular oxygen in DMA/H_2O solutions containing $PdCl_2$ (Table 2, runs 2–4). The industrially important fragrance ketones and aldehydes were obtained in near 90% combined yields, with the ketones accounting for 70–85% of the mass balance (Scheme 1 and Scheme 2). Although the values for the initial rates for all four substrates are close, the reactions with methyleugenol, safrole, and estragole need more time to be completed than that with eugenol. The relative amounts of the corresponding aldehydes, especially of the one derived from estragole, are larger than in the case of eugenol (Table 2, run 1), so that the selectivities for the ketones are lower, but the reaction variables have not been optimized yet.

Table 2. Palladium-catalyzed oxidation of eugenol (**1a**), methyleugenol (**2a**), safrole (**3a**), and estragole (**4a**) in dimethylacetamide (DMA) by molecular oxygen.[a]

Run	Substrate	Time [h]	Conversion [%]	Rate[b] [10^{-2} M·h^{-1}]	Selectivity [%]		
					Ketone **1b**–**4b**	Aldehyde **1c**–**4c**	Total[c]
1	eugenol (**1a**)	4	100	6.4	90	7	97
2	methyleugenol (**2a**)	7	97	6.2	80	11	91
3	safrole (**3a**)	7	95	7.0	86	8	94
4	estragole (**4a**)	7	97	6.0	72	19	91

[a] *Conditions:* [substrate] = 0.20 M; [$PdCl_2$] = 0.005 M; 60 °C; gas phase O_2, 10 atm; solvent DMA/H_2O (20 vol%); conversion and selectivity were determined by GC and based on the consumed substrate.
[b] Initial rate of the substrate conversion.
[c] Total selectivity for corresponding ketone and aldehyde.

Conclusions

In summary, we have reported a novel and efficient method for the oxidation of naturally occurring allylbenzenes into the corresponding methyl ketones, under mild aerobic conditions. The use of renewable biomass-based feedstock substrates, low-cost high boiling solvents, and molecular oxygen as the final oxidant are especially relevant to the green chemistry concept. It is also important that $PdCl_2$ operates as the sole, recyclable catalyst and the reaction does not require co-oxidants, often corrosive, which must be employed in the conventional palladium-catalyzed oxidations of alkenes. This simple and clean catalytic method represents an attractive synthetic pathway to the compounds of industrial importantance for the flavour and pharmaceutical industries. Further studies are targeted towards the development of solid palladium catalysts resistant to leaching in polar solvents in order to facilitate catalyst separation.

Experimental Section

General Remarks

All reagents were purchased from commercial sources and used as received. The reactions at atmospheric pressure were carried out in a magnetically stirred glass reactor and followed by measuring dioxygen uptake and by gas chromatography (GC). The reactions at higher pressures were carried out in a magnetically stirred stainless steel 100-mL reactor (autoclave) and followed by GC.

NMR spectra were recorded in $CDCl_3$ using a Bruker 400 MHz spectrometer, with TMS as an internal standard. Mass spectra were obtained on a Shimadzu QP2010-PLUS instrument operating at 70 eV.

Typical Procedure

In a typical run, the solution of the substrate, $PdCl_2$ and bornyl acetate (internal standard, 0.1 M) in the mixture of amidic solvent with water in the indicated proportions (20 mL) was transferred into the reactor. Concentrations of the components are given in Table 1 and Table 2. The glass reactor was connected to a gas burette containing molecular oxygen to measure the gas uptake. The autoclave was pressurized with oxygen to the total pressure indicated in Table 1 and Table 2. The reactors were placed in an oil bath; then, the solutions were stirred at the specified temperature. At appropriate time intervals, aliquots were taken *via* special sampling systems without depressurization of the reactors and analyzed by GC using a Shimadzu 17A instrument fitted with a Carbowax 20 m capillary column and a flame ionization detector. After carrying out the reaction and cooling to room temperature, the excess of oxygen was slowly vented from the autoclave. The products were isolated by a column chromatography (silica gel 60) using mixtures of hexane and CH_2Cl_2 as eluents and identified by ^1H, and ^{13}C NMR and/or GC-MS.

Acknowledgements

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