Palladium–Hydroquinone Catalysed Electrochemical 1,4-Oxidation of Conjugated Dienes

Jan-E. Bäckvall* and Adolf Gogoll

Department of Organic Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala, Sweden

The mediator system palladium(II)–hydroquinone was shown to catalyse the anodic oxidation of cyclohexa-1,3-diene in acetic acid to produce selectively either *trans*- or *cis*-1,4-diacetoxycyclohex-2-ene (**1**) depending on the conditions.
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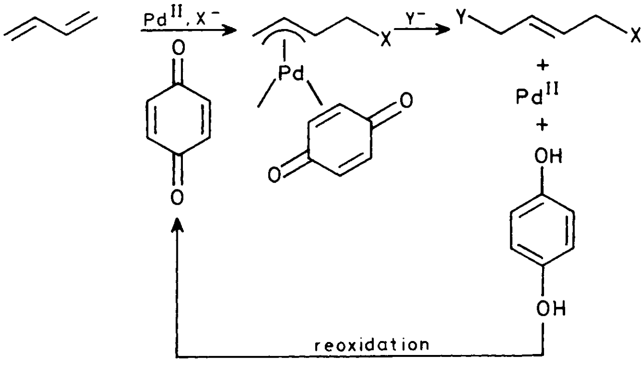
We have recently developed a number of palladium catalysed 1,4-oxidations of conjugated dienes (Scheme 1).[1,2] In all these oxidations *p*-benzoquinone plays an important role as both an oxidant and as a ligand. The benzoquinone was found to have a unique ability to direct the reaction towards a high selectivity, and attempts to replace it with oxidants having an equal or higher oxidation potential led to either no reaction or a less selective reaction.[1a,b] One way to replace the benzoquinone as the ultimate oxidant and still make use of its favourable properties is to use it in catalytic amounts and reoxidize the hydroquinone formed in each cycle.[1,3] Since hydroquinone–benzoquinone has a well defined electro-

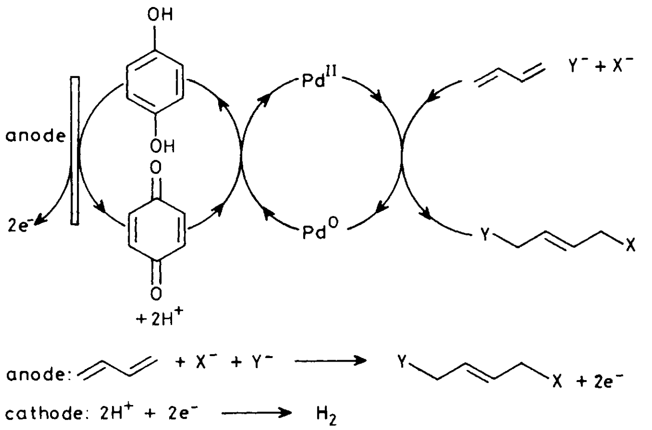
Table 1. Electrochemical oxidations of cyclohexa-1,3-diene using a Pd–hydroquinone catalytic system.[a]

Entry	Anode	$[Pd(OAc)_2]$ /mM	LiCl /mM	Time /h	Turnover on Pd[b]	% Yield of (**1**)[c]	% Current yield[c]	Ratio *trans* : *cis*[d]
1	Pt	5	—	12	15	53(69)	74(96)	91 : 9
2	Pt	31	—	25	26	61(74)	67(81)	86 : 14
3	Pt	31	—	48	46	39(49)	67(85)	87 : 13
4	Ti/MnO_2[e]	14	—	7.5	6.1	65(64)	48(47)	89 : 11
5	Ti/MnO_2[f]	30	—	24	30	58(72)	50(62)	86 : 14
6	Pt	19	75	29	7.3	34(39)	40(46)	10 : 90
7	Pt	5	26	37	6	29(41)	61(63)	11 : 89
8	Ti/MnO_2[f,g]	46	—	3.5	5.6	49	40	83 : 17

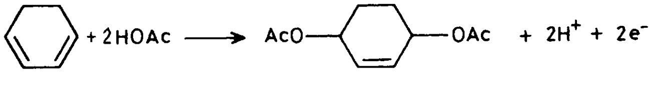
[a] The reactions were performed in acetic acid using $Pd(OAc)_2$ and hydroquinone as catalysts. Lithium acetate concentrations of 1 M were used except in entries 6 and 7 where 0.7 and 2.5 M were used respectively. Hydroquinone concentration was 5.6 × $[Pd(OAc)_2]$ except entries 1 {1.8 × $[Pd(OAc)_2]$} and 7 {4 × $[Pd(OAc)_2]$}. Unless otherwise noted a divided cell was used. [b] Turnovers based on g.c. yields. [c] Refers to isolated yields; figures in parentheses refer to g.c. yields. [d] Determined by ^1H n.m.r. and h.p.l.c. [e] An undivided cell was used. [f] Without potential control. [g] Performed in HOAc–H_2O 1 : 1.



Scheme 1. Palladium catalysed 1,4-oxidation of conjugated dienes.

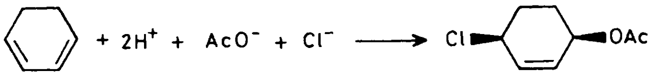


Scheme 2



(**1**)

Scheme 3. 1,4-Diacetoxylation of cyclohexa-1,3-diene.



(**2**)

Scheme 4. 1,4-Acetoxychlorination of cyclohexa-1,3-diene. *Reagents:* cat. $Pd(OAc)_2$, cat. hydroquinone, LiCl, LiOAc, $LiClO_4$, HOAc, anodic oxidation.

chemistry[4], it occurred to us that anodic oxidation would be suitable for the reoxidation of hydroquinone in these palladium catalysed reactions. Here we report our preliminary results on an electrochemical 1,4-oxidation of conjugated dienes mediated by Pd^{II}–hydroquinone.

The principle for the electrochemical process used is shown in Scheme 2. The hydroquinone is used as a mediator[5] for the electron transfer. In this way an efficient reaction takes place at anodic potentials of <1 V [*vs.* standard calomel electrode (S.C.E.)]. At the cathode, protons are reduced to hydrogen.

The experiments were performed in acetic acid with $LiClO_4$ as supporting electrolyte using $Pd(OAc)_2$ and hydroquinone as catalysts. Lithium acetate was added in all experiments. All model oxidations were carried out on cyclohexa-1,3-diene. We first tried to use an undivided cell with a platinum anode and a steel cathode. This led to conversion, but the current yield was typically <30% and furthermore, palladium was deposited on the cathode thus removing the catalyst. We therefore divided the cell into anodic and cathodic compartments using a G3-filter. This considerably improved the current yield to *ca.* 90%.

Results from electrochemical oxidations of cyclohexa-1,3-diene using the Pd–hydroquinone catalytic system are given in Table 1. Catalysing the electron transfer by the redox couple hydroquinone/benzoquinone makes it possible to keep the anodic potential very low.† In entries 1—4 and 6,7 the anodic potential was kept between 0.7 and 0.8 V (*vs.* S.C.E.). This resulted in a mild and selective reaction. Although the current density at these potentials was modest, experiments on a preparative scale were performed without any problems. For example, in the experiments in entries 2 and 3, which were run in a 20 ml volume using a 40 cm^2 platinum anode, the amounts of diacetate produced were 2.7 and 4.5 g respectively. The current density in both cases was 1.4—1.5 mA/cm^2. As can be seen from entry 3, turnover numbers of up to 46 can be obtained.

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† Current–potential curves showed that the half-wave potential for the hydroquinone oxidation (at a Pt anode) is +0.9 V *vs.* S.C.E., whereas the half-wave potential for the direct oxidation of the π-allyl complex is +1.1 V *vs.* S.C.E.

In an attempt to replace the platinum anode with a less expensive material we tried the Ti/MnO_2 anode.[6] Interestingly, this anode gave an almost 50% current yield in an undivided cell when a steel wire with a small active area was used as cathode. In a divided cell with a constant cell voltage of 30 V (which gave an anode potential of 1—1.5 V *vs.* S.C.E.) a comparable result to that of entry 2 was obtained. The current density was 4 mA/cm^2 and 4.4 g of diacetate were produced in a 20 ml volume.

The electrochemical oxidation also worked in the presence of chloride ions (entries 6 and 7, Table 1). This is of synthetic importance since chloride ligands are known to have a drastic effect on the stereochemical outcome of the reaction.[1b] The use of catalytic amounts of lithium chloride afforded the *cis*-diacetate as the major product, with a *cis–trans* selectivity of 90 : 10. This is a slightly lower selectivity than that obtained with chemical oxidation.‡ In the presence of catalytic amounts of LiCl the current density dropped significantly.§

It is known that the 1,4-diacetoxylation changes to a 1,4-acetoxychlorination if the chloride ion concentration is further increased. We therefore performed an electrochemical oxidation of cyclohexa-1,3-diene at a much higher chloride concentration. This led to a selective formation of (**2**) in 46% isolated yield (*cis* : *trans* = 86 : 14) (Scheme 4).

It is likely that the Ti/MnO_2 electrode used in the oxidations has a catalytic surface consisting of the redox couple MnO_2/Mn_2O_3 ($2MnO_2 + 2H^+ + 2e^- \rightleftarrows Mn_2O_3 + H_2O$). The very active MnO_2 is expected to oxidize hydroquinone to *p*-benzoquinone and the Mn_2O_3 formed on the surface would be electrochemically reoxidized to MnO_2. Thus, the system would constitute another example of 'triple catalysis'[7] involving the redox catalysts MnO_2/Mn_2O_3–benzoquinone/hydroquinone–Pd^{II}/Pd^0.

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‡ In the MnO_2–benzoquinone oxidized diacetoxylation in the presence of catalytic amounts of chloride a *cis-trans* ratio of 96 : 4 was obtained.[1b]

§ In the presence of catalytic amounts of chloride the palladium catalysed cycle is slower than in the chloride free case. This results in a much lower steady state concentration of hydroquinone, to which the current is proportional.