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Synthesis of Substituted Benzoquinones and their Use for Mediated Electrochemical Conversions

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Hydroxy- (**1a–3a**) and hydroxyalkyl-substituted benzoquinones (**6a–8a**, **27a**), suited to be immobilized by esterification with polyacrylic acid, are prepared. Their cathodic reduction potential $E_{p,c}$ (1) correlates linearly with their substituent constant. The cathodic reduction of dioxygen and the palladium(II)-catalyzed anodic oxidation of alkenes are mediated by the benzoquinones **7b**, **8b** and **27b**, respectively.

Compared to chemical oxidations anodic oxidations offer advantages. These include: simple reaction conditions that can be flexibly applied, easy scale-up, low cost and low hazard to the environment due to the avoidance of using toxic transition metal oxidation reagents[2]. The electrode has the further advantage of potential selectivity, but sometimes lacks the chemoselectivity of chemical oxidants. This can be gained in indirect electrolyses, where an electrocatalyst mediating the selective transformation is continuously regenerated at the electrode[3]. A further improvement of this mode of electrolysis is possible, if the electrocatalyst is immobilized at the electrode surface. There are numerous applications of electrodes modified with mediators on an electroanalytical scale[4]. However, only few applications on a preparative scale[5] are described. Monolayers of mediators can be fixed at the electrode surface by covalent bonds. This is achieved by reaction of trimethoxy(alkylamino)silanes with hydroxy groups of the electrode surface and fixation of the electroactive groups at the amino substituent[6]. Modifications of higher stability are achieved by the coverage of the electrode surface with polymer compounds. Conducting polymers[7] like polypyrrole and polymers with localized redox centers[4a] are used. The polymer layers are produced by dip coating, spin coating, droplet evaporation, and electropolymerization[4a].

The aim of this work, described in this and a subsequent paper, is the use of benzoquinones as catalysts for electrochemical conversions and their immobilization at the electrode surface by covalent binding to a polymer. Reasons for their choice are their well investigated electrochemistry[8], their frequent use as oxidants in organic synthesis[9], and the fact that they have already been used as mediators at polymer-modified electrodes[10]. In this work benzoquinones are covalently attached to the polymer by way of an ester function. The preparation of *p*-benzoquinones bearing a hydroxylalkyl group, their redox behavior, and the use of benzoquinones as mediators in homogeneous indirect electrolysis are described. A subsequent paper will report on the esterification of these substituted benzoquinones with polyacrylic acid, the coating of these polyacrylates to the electrode surface and the electrochemistry of these modified electrodes.

Synthesis of Hydroxy- and Hydroxyalkyl-Substituted Benzoquinones

The *p*-benzoquinones **1a–3a** and **6a–8a**, which bear hydroxy groups either at the quinone ring or in the side chain, should be suited to be attached to polyacrylic acid by means of an ester bond.

Compound **3a** is obtained in 78% yield by treatment of tetrachloro-*p*-benzoquinone with dilute aqueous sodium hydroxide[11] at 0°C. At 80°C benzoquinone **2a** is obtained in 80% yield instead[12]. Benzoquinone **1a** is prepared in 35% yield by arylation of *p*-benzoquinone with the diazonium salt of *p*-hydroxyaniline[13]. For the investigation of the electrochemical behavior of the esters of **1a–3a** with polyacrylic acid the corresponding propionates **1b–3b** have been taken as model compounds. They have been prepared by the reaction of **1a–3a** with propionyl chloride in the presence of triethylamine at room temperature.

A sulfonyl substituent increases the oxidation power of benzoquinones. Furthermore, it is suited to link the benzoquinone to a polymer bearing phenyl groups. For this reason the benzoquinone **4** has been prepared. Benzoquinone is treated with sodium benzenesulfinate to afford in 83% yield 2-(phenylsulfonyl)-*p*-hydroquinone (**5**)[14], which is oxidized with silver carbonate in toluene to afford in 82% yield the desired benzoquinone **4**.

In order to vary the distance between the polymer backbone and the mediator the hydroxyalkyl-substituted benzo-

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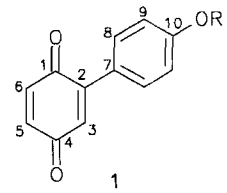

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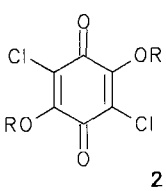
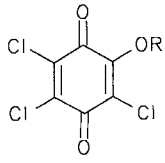
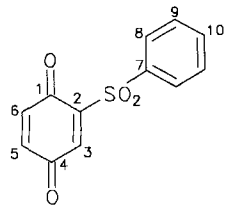


2

1,2	R
a	H
b	COC_2H_5
c	COC_6H_5



3	R
a	H
b	COC_2H_5



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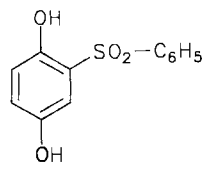
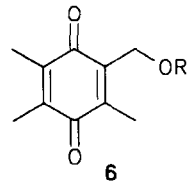


5

quinones **6a**–**8a** have been chosen, which have different distances between the hydroxy group and the benzoquinone part. Their synthesis is achieved by a strategy applied to the preparation of ubiquinone and menaquinone analogues[15]: A lithiated hydroquinone dimethyl ether is allowed to react with an electrophilic carbon fragment. 2,3,5-Trimethyl-*p*-hydroquinone (**9**) is methylated with dimethyl sulfate in the presence of potassium carbonate in acetone to afford in 77% yield the dimethoxy compound **10** (eq. 1).

Compound **10** is converted into the bromo compound **11** in 99% yield by bromination in dichloromethane. Halogen/metal exchange in **11** with butyllithium affords the lithiated aryl compound **12**, which is carboxylated to furnish in 71% yield the benzoic acid **13**, that is reduced with $LiAlH_4$ in 94% yield to give the benzyl alcohol **14a**. (2-Hydroxypropyl)benzene **15a** is obtained in 74% yield by nucleophilic attack of **12** at propylene oxide. Transmetalation of **12** with copper iodide/dimethyl sulfide and reaction of the arylcopper compound with allyl bromide affors the allylbenzene **16**, that is subsequently converted by hydroboration and oxidation with hydrogen peroxide into the alcohol **17a** in 59% overall yield. As side product the regioisomer **15a** is detected in a ratio **17a**/**15a** of 12:1 by GLC. The propionates **14b**, **15b** and **17b** are prepared from **14a**, **15a** and **17a** by treatment with propionyl chloride in pyridine in 87 to 95% yield. The careful oxidation of **14b**, **15b** and **17b** is achieved by oxidation with silver(II) bis(2,6-dipicolinate) according to the procedure of Kloc[16]. With this oxidant the hydroquinone dimethyl ethers are converted in 63 to 75% yield into the corresponding quinones **6b**–**8b**.

For the preparation of larger amounts of these benzoquinones the use of the silver(II) salt is too expensive. Therefore, the anodic oxidation of suitably substituted hydroquinone dimethyl ethers has been explored as an alternative. This method has been used for the oxidation of some hydroquinone dimethyl ethers to the corresponding quinone bisketals[17]. As this method is not suited for the oxidation of compounds with hydroxy groups and as it has been found that the propionates are partially hydrolyzed under the reaction conditions of the oxidation, the corre-



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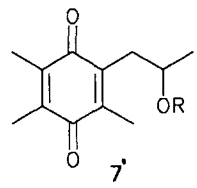

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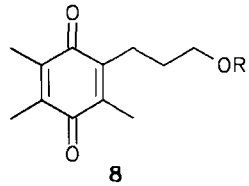
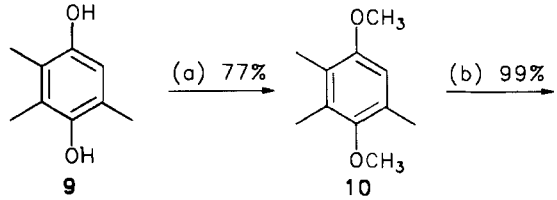


8

6-8	R
a	H
b	COC_2H_5



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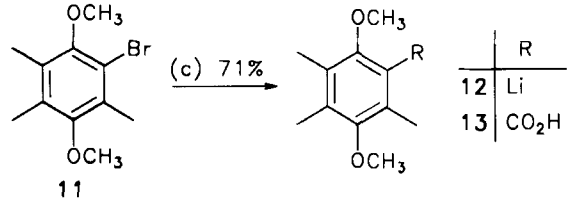
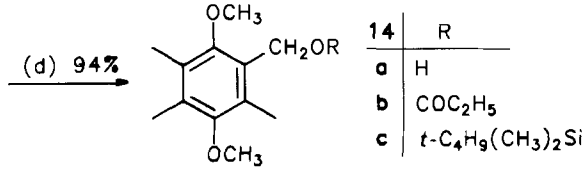


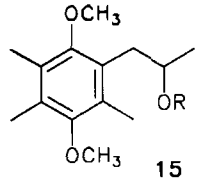
11

R	
12	Li
13	CO_2H



14	R
a	H
b	COC_2H_5
c	t-$C_4H_9(CH_3)_2Si$

(a): $(CH_3)_2SO_4$, K_2CO_3; (b): Br_2,Fe; (c): 1.*n*BuLi, 2. CO_2; (d): $LiAlH_4$.



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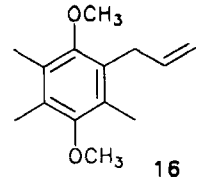

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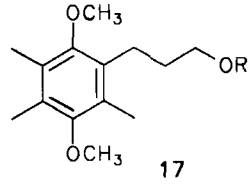
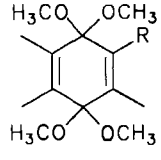


17

15,17	R
a	H
b	COC_2H_5
c	t-$C_4H_9(CH_3)_2Si$



	R
18	$CH_2OTBDMS$
19	$CH_2CH(CH_3)OTBDMS$
20	$(CH_2)_3OTBDMS$

sponding *tert*-butyldimethylsilyl (TBDMS) ethers have been used instead. **14a**, **15a**, and **17a** are converted in 87–96% yield into the corresponding TBDMS ethers **14c**, **15c** and **17c** by the reaction with *tert*-butyldimethylsilyl chloride (TBDMSCl) and imidazol[18]. The TBDMS ethers are oxidized in methanol/potassium hydroxide at a platinum anode to afford in 67–72% yield the corresponding quinone biseketals **18**–**20**, which are hydrolyzed with dilute hydrochloric acid in acetone to give the quinones **6a**–**8a**. These are clearly identified by their spectroscopic data. Compound **7a** has been formed also as a side product in the photolysis of tetramethyl-1,4-benzoquinone[19]; **8a** has been prepared before by another route[20].

The monoalkylated hydroxyquinone **27a** is synthesized by the reaction of benzoquinone with trialkylborane[21]. For that purpose allyl alcohol is protected with TBDSMCl with formation of **21** (eq. 2a), which is then transformed with borane into the alkylborane **22**. Upon addition of *p*-benzoquinone (**23**) the hydroquinones **24a**, **b** are obtained. The isomer ratio of **24a**:**b** is 6:1 (determined by GLC integration). This, for the case of hydroborations, only moderate regioselectivity has two reasons. Firstly, the electronegativity of oxygen disfavors the terminal addition of the borane[22]; secondly, in the reaction with benzoquinone the secondary alkyl group is preferentially transferred in a radical reaction[23]. Since **24a** and **b** cannot be separated by column chromatography, they are directly oxidized with silver carbonate to the quinones **25** and **26**, which can be separated without problems. Analytically pure samples of **24a**, **b** are obtained by reduction of the separated quinones **25** and **26**. Then **25** is hydrolyzed with aqueous HCl in acetone to **27a**, which is converted with propionyl chloride into the corresponding propionate **27b**.

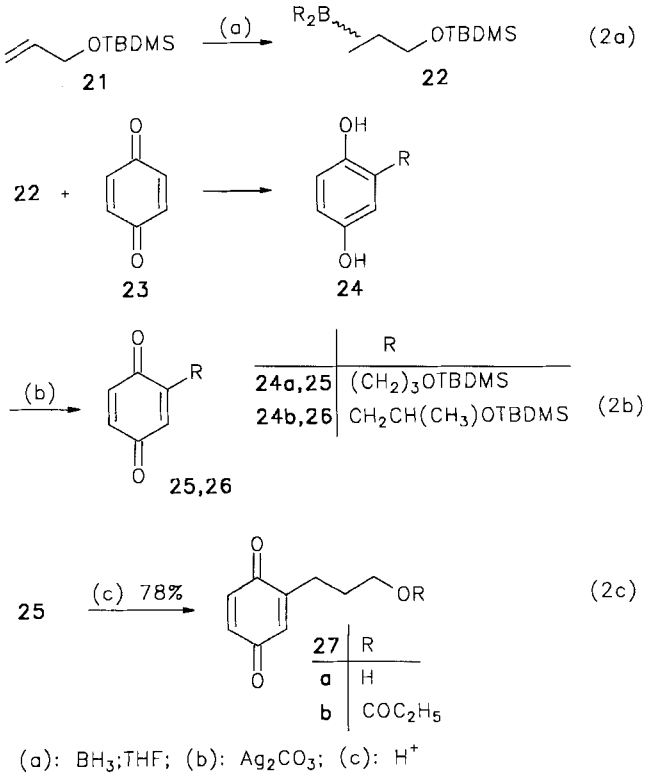
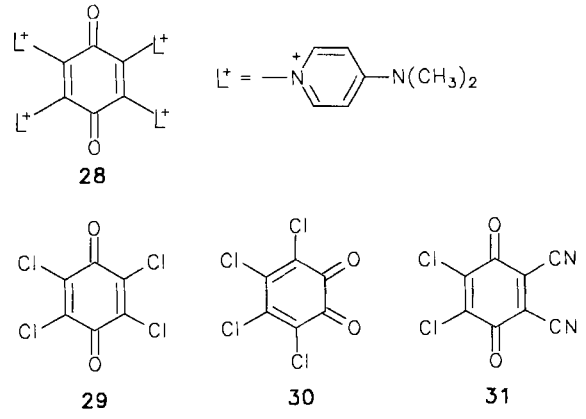


Table 1. First cathodic peak potential of substituted benzoquinones[a]

Quinone	1a	1b	2a	2b	3a	3b	4	28
$-E_{p,c}$ [V]	0.87	0.86	0.49	0.42	0.37	0.39	0.50	-0.16
Quinone	23	29	30	31	6b	7b	8b	27b
$-E_{p,c}$ [V]	0.89	0.35	0.25	-0.16	1.10	1.23	1.25	0.96

[a] Working electrode: platinum; reference electrode: Ag/0.1 M Ag^+, scan rate: 0.1 V/s, electrolyte: 0.1 TBAP in CH_3CN, quinone concentration: $2.5 \cdot 10^{-3}$ M, **28** saturated solution; reproducibility ±20 mV.



Cyclic Voltammetry of the Benzoquinones

The behavior of *p*-benzoquinones in polarography and cyclic voltammetry in aprotic media has been studied in several cases[24]. They are reduced in two one-electron transfers first to the semiquinone anion and then to the hydroquinone dianion. With the exception of the hydroxy-substituted benzoquinones **1a**–**3a** and **27a** the other benzoquinones, prepared here, show an analogous behavior. The deviation of the hydroxy-substituted benzoquinones can be attributed to their acidity[24a], which leads to additional proton transfers and hydrogen bond effects. In Table 1 the first cathodic peak potentials [$E_{p,c}$ (1)] of the prepared benzoquinones and those of some additional ones are compiled. The difference to the reverse anodic peak potential $E_{p,a}$ is about 70 to 100 mV. Similar results have been found in the polarography of *p*-benzoquinones in acetonitrile[24c]. For the evaluation of the oxidation power of a quinone the correlation of its polarographic half-wave potential with the Hammett substituent parameter can be taken[24a]. For the use of data from cyclic voltammetry a modified correlation (eq. 3) can be employed[24a,25].

$$E_{p,c} = p \cdot \sigma + C \qquad (3)$$

p: constant for the redox reaction quinone/semiquinone anion, σ: substituent constant[26], *C*: constant

Figure 1 shows the plot of the first cathodic reduction potentials [$E_{p,c}$ (1)] of the benzoquinones against their substituent constants. For benzoquinones with several substituents the sum of their substituent constants is taken. The straight line has been calculated by application of the least-squares method[27]. The quinones **2a**, **b** and **3a**, **b** are ex-

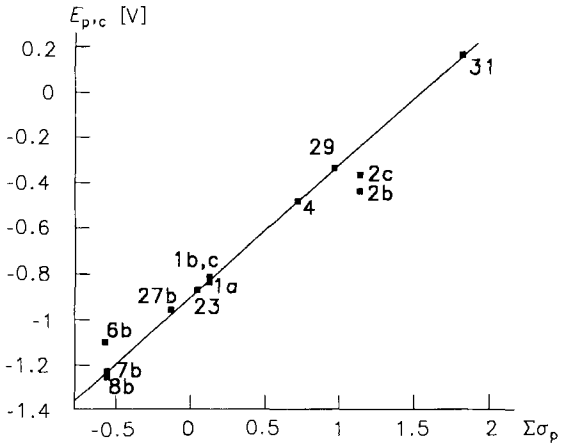


Figure 1. Correlation of $E_{p,c}$ values of benzoquinones with their Hammett substituent parameters. Conditions: platinum cathode, Ag/0.1 M Ag^+ reference electrode, scan rate: 0.1 V/s, 0.1 M TBAP in acetonitrile, quinone concentration: $2.5 \cdot 10^{-3}$ M

cluded in this correlation. As numerical expression of the straight line eq. (4) has been obtained.

$$E_{p,c}\,(1)\,(V) = 0.589\,(V)\,\sigma - 0.89\,(V) \qquad (4)$$

The hydroxyquinones **2a** and **3a** deviate significantly from the straight line. This can be attributed to the stabilization of the formed semiquinone anion by an intramolecular hydrogen bond[24a].

Anodic Reoxidation of Substituted Hydroquinones

For an oxidation with quinones as electrocatalysts it is necessary that the resulting hydroquinone is regenerated to a high extent at the anode. The oxidation potentials of some hydroquinones are compiled in Table 2.

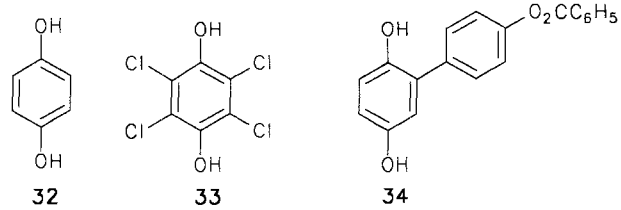


Table 2. Oxidation peak potentials of substituted hydroquinones[a]

Hydroquinone	5	32	33	34
$E_{p,a}$ [V]	1.00	0.62	0.97	0.58

[a] Conditions: platinum anode, reference electrode: Ag/0.1 M Ag^+, electrolyte: 0.1 M TBAP in acetonitrile, scan rate: 0.1 V/s.

At 0.62 V (vs. Ag/0.1 M Ag^+) **32** is oxidized in an irreversible two-electron process to benzoquinone[24a]. The mechanism is not fully established yet. It is assumed that **32** is oxidized by electron transfer and deprotonation to the semiquinone. By way of cyclic voltammetry its coupling product, a benzoquinone-hydroquinone semiacetal, may be generated as intermediate, that is subsequently rapidly cleaved into benzoquinone and hydroquinone[28].

In a preparative-scale electrolysis in acetonitrile **32** is oxidized in good yield to benzoquinone[28]. The potential-controlled electrolysis of the hydroquinones **5**, **32**–**34** is performed in a divided cell at platinum electrodes. The results are compiled in Table 3.

Table 3. Controlled potential anodic oxidation of selected hydroquinones

Hydroquinone	Supporting electrolyte[a]	Potential vs. Ag/0.1 M Ag^+ [V]	Yield[b] (%)	Current yield[b] (%)
32	$LiClO_4$	0.9	45.3	71.5
33	TBAP	1.2	80.7	85.7
33	$LiClO_4$	1.2	84.0	95.3
34	$LiClO_4$	0.8	76.1	94.4
5	$LiClO_4$	1.1	61.2	63.8

[a] 0.1 M solutions in acetonitrile. – [b] The yield is calculated based on hydroquinone, the current yield on current consumption.

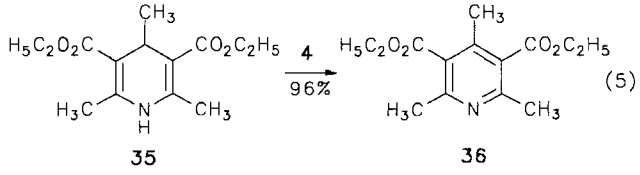
As supporting electrolyte $LiClO_4$ has proved to be more efficient than tetrabutylammonium perchlorate (TBAP). With TBAP as supporting electrolyte in the oxidation of **33** a side product is formed, that cannot completely be separated from the benzoquinone **29**. The lower yields in the case of **32** and **5** are due to losses during workup. The results show that the hydroquinones can be oxidized in acetonitrile in good yields to the corresponding benzoquinones.

Electrochemical Conversions Mediated by Benzoquinones

In the following the use of benzoquinones as mediators is explored. For that purpose reactions with benzoquinones as oxidant or benzoquinone radical anions as reductant are investigated.

Dehydrogenation of 1,4-Dihydropyridine 35

Benzoquinones are frequently used as dehydrogenation reagents[29]. Benzoquinone **29** oxidizes diethyl 1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate nearly quantitatively to the corresponding pyridine[29a]. This dehydrogenation has been extended to quinone **4**. It oxidizes in acetonitrile as solvent diethyl 1,4-dihydro-2,4,6-trimethylpyridine-3,5-dicarboxylate (**35**) in 96% yield to the corresponding pyridine **36** (eq. 5).



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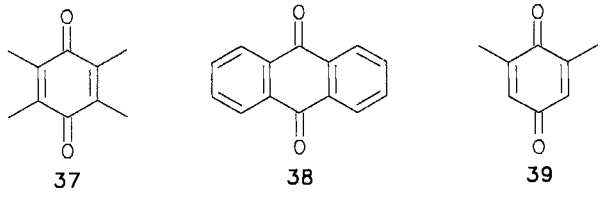
In orientating experiments we have not succeeded in oxidizing **35** with the quinones **1b** and **2b**, although **2b** is a stronger oxidant than **4**.

Quinone-Mediated Cathodic Reduction of Dioxygen

The cathodic reduction of dioxygen is catalyzed at cathodes being modified with polymers bearing anthraquinone[10b,30] and 1,4-naphthoquinone units[10d,e]. Tetramethyl-1,4-benzoquinone (**37**) ($E_{p,c} = -1.31$ V), **6b** ($E_{p,c}$ =

−1.10 V), **7b** ($E_{p,c}$ = −1.23 V), and **8b** ($E_{p,c}$ = −1.25 V) have reduction potentials that are similar to that of anthraquinone (**38**) ($E_{p,c}$ = −1.37 V, CH_3CN, 0.1 M TBAP vs. Ag/0.1 M Ag^+). Whilst in dimethyl sulfoxide no catalytic effect has been observed in the reduction of dioxygen, catalysis has been found to occur in acetonitrile as solvent (Figure 2). For each of the quinones **8b**, **37**, and **38** three cyclic voltammetry curves are shown. The first curve corresponds to the reduction of dioxygen at platinum in the absence of the quinone, the second one in the presence of the quinone, and the third one in the absence of dioxygen.



37 38 39

Dioxygen is reduced in acetonitrile at platinum at peak potentials between −1.9 to −2.1 V vs. Ag/0.1 M Ag^+. The cyclic voltammetry curve is similar to that described for untreated platinum[31]. The relative small reoxidation peak ($i_{p,a}/-i_{p,c}$ = 0.2 to 0.3) points to irreversible consecutive reactions of the superoxide anion.

In the presence of the benzoquinones the reduction potential of dioxygen is anodically shifted. The shift decreases from **38** (ΔE = 0.36 V) via **37** (ΔE = 0.31 V) to **8b** (ΔE = 0.23 V). Compound **7b** shows an analogous behavior as **8b**, whilst **6b** exerts no influence on the dioxygen reduction. This result indicates that the rate of electron transfer between quinone and dioxygen decreases in the above order[32]. The reduction potential for **6b** is with −1.10 V too much anodic, which explains the missing electrocatalytic activity of **6b**. The results are qualitatively in accord with kinetic data obtained by pulse radiolysis[33] for the electron transfer between the quinone radical anion and dioxygen. Here for **23** ($E_{p,c}$ = −0.89 V) and **39** ($E_{p,c}$ = −1.03 V) the forward rate constant is 10^2 times smaller than the backward rate constant, whilst the reverse holds for **37** ($E_{p,c}$ = −1.31 V).

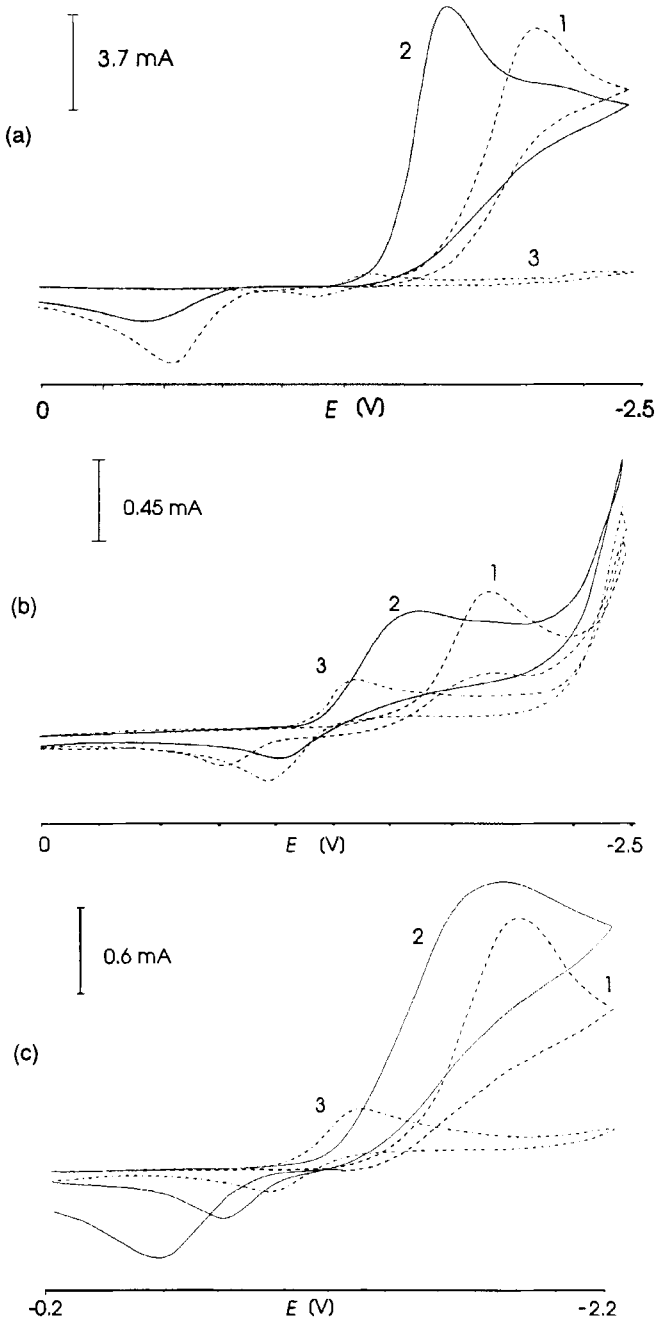


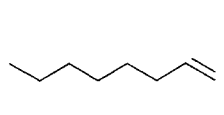
Figure 2. Dioxygen reduction mediated by **8b**, **37**, and **38**. Conditions: platinum cathode, Ag/0.1 M Ag^+ reference electrode, 0.1 M TBAP in acetonitrile. (a) Mediator: **38**; (b) mediator: **37**; (c) mediator: **8b**. Curve 1, electrolyte saturated with dioxygen, curve 2, electrolyte saturated with dioxygen and addition of quinone (about $2 \cdot 10^{-3}$ M), curve 3, electrolyte with quinone degassed with argon

Palladium-Catalyzed Anodic Oxidation of Alkenes Mediated by Benzoquinones

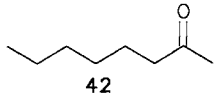
Terminal, internal, and cyclic alkenes can be oxidized by palladium(II) catalysis[34]. 1-Alkenes are converted in this manner in the presence of water to 2-alkanones[35]. Also other nucleophiles such as alcohols or carboxylic acids can be introduced in this way[36]. Palladium(II) can be regenerated by $CuCl/O_2$, which, however, can lead to the formation of chlorinated side products. This has made the development of alternative oxidants for the regeneration of palladium(II) attractive[38]. Such an oxidant is benzoquinone[39], which is regenerated by manganese(IV) oxide[40], dioxygen[39], or anodic oxidation[41–45]. Thus, for the palladium(II)-catalyzed oxidation of alkenes the use of polymer-modified electrodes with immobilized benzoquinones might be of interest. In our case, the oxidation of 1-alkenes **40** and **41** has been studied. The results described in ref.[41–45] were supplemented by additional experiments to find suitable electrolysis conditions for the use of the substituted benzoquinones as mediators.

Optimization of the Catalyzed 1-Octene (**40**) *Oxidation:* 1 equiv. of **40** is allowed to react with $PdCl_2$ and 1.1 equiv. of *p*-benzoquinone (**23**), and the yield of 2-octanone (**42**) is determined by calibrated GLC. Table 4 summarizes the

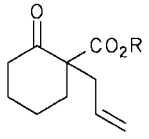
dependence on the solvent variation. DMF proves to be the most suitable solvent. The result is comparable with that obtained for the 1-dodecene oxidation to 77% 2-dodecanone, where palladium(II) is also regenerated by benzoquinone[46]. Acetone is also an appropriate choice, but its electrochemical properties are less advantageous than those of DMF. The influence of the water concentration on the yields is shown in Figure 3. The yield of **42** is only slightly dependent on the water concentration, a maximal yield is observed at a ratio DMF/water of 9:1. In the regeneration with $CuCl/O_2$ the dependence on the water content is much more pronounced.



40



42



41	R
a	C_2H_5
b	CH_3

Table 4. Solvent dependence of the Pd(II)-catalyzed 1-octene (**40**) oxidation[a]

Solvent	DMSO	CH_3CN	Acetone	DMF
Yield of **42** (%)	14	48	77	87

[a] Reaction conditions: 1 mmol of **40**, 1.1 mmol of **23**, 0.1 mmol of $PdCl_2$, solvent/water (10:1), room temp.

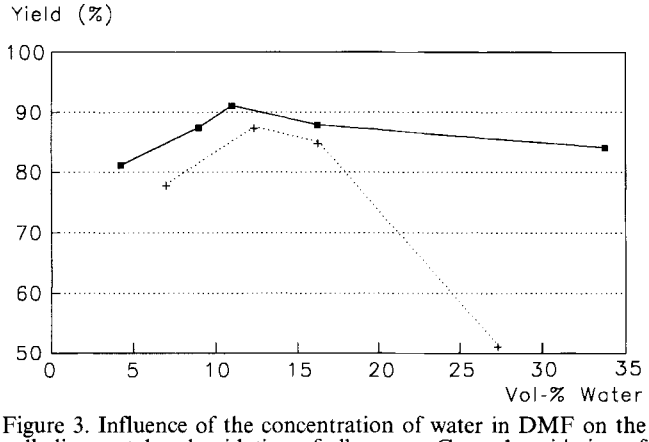
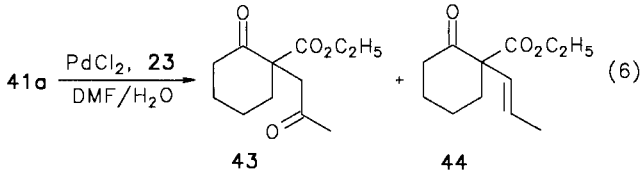


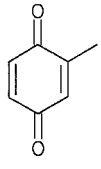
Figure 3. Influence of the concentration of water in DMF on the palladium-catalyzed oxidation of alkenes. – Curve 1, oxidation of **40** with **23**, curve 2, oxidation of 1-dodecene with $CuCl/O_2$[37]

The amount of $PdCl_2$ can be decreased to 0.05 equivalents, still lower concentrations lead to diminished yields. An up-scale to 25 mmol of **40** causes no problems, **42** can be isolated in 83% yield in this case.

Oxidation with Alkylbenzoquinones: Alkylbenzoquinones have been investigated as cooxidants, because the alkyl chain is needed to bind them later to the polymer that is coating the electrode. In addition to **40**, we have also oxidized **41a**. With benzoquinone as cooxidant **41a** is converted to 87% of diketone **43** and 9% of isomerized starting material **44** (eq. 6). Isomerization of double bonds in the presence of palladium(II) salts have been described[38a]. Table 5 summarizes the results of the oxidation of **40** and **41a**.



43 **44**



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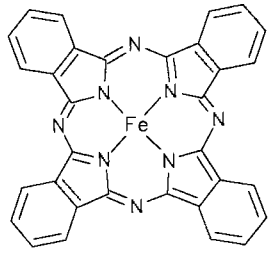

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Table 5. Palladium(II)-catalyzed oxidation of the alkenes **40**, **41a** with substituted benzoquinones[a]

Quinone	Yield of **42** (%)	Yield of **43** (%) [mass balance (%)]	Temp.
23	91	87(96)	room temp.
4	11	--	room temp.
4	22	--	60°C
29	36	8(77)	room temp.
2b	13	--	room temp.
2c	7	--	room temp.
1b	82	77(82)	room temp.
1b	83	--	60°C
1c	51	67(74)	room temp.
1c	74	--	60°C
28	11	--	room temp.
45	--	86(91)	room temp.
39	--	78(89)	room temp.
37	--	24(87)	room temp.

[a] Reaction conditions: 1 mmol of **40** or **41a**, 0.05 mmol of $PdCl_2$, 1.1 mmol of quinone, 2 ml of DMF/water (8:1).

Table 5 shows that the use of quinones **1b**, **23**, **39**, and **45** leads to satisfactory yields of the corresponding ketones. The moderate yield with **1c** seems to be due to its low solubility in the solvent; in this case the conversion can be increased at 60°C. The other quinones furnish low yields of the ketones. Thus, in the subsequently performed experiments only **1b**, **23**, and the monoalkylated quinone **27b** are used as cooxidants.

Electrochemical Regeneration of the Cooxidant: In the course of the olefin oxidation the cooxidant benzoquinone is reduced to hydroquinone. The cyclic voltammetry curve of **32** exhibits an irreversible anodic peak potential ($E_{p,a}$) at 0.82 V (vs. SCE) in DMF/water (8:1, 0.1 M $LiClO_4$). The curve is comparable to that in acetonitrile, where the oxidation of **32** leads to **23**. The direct oxidation of **40** can be excluded, as also in the presence of $PdCl_2$ no oxidation peak is detectable below 1.2 V vs. SCE.

The preparative-scale electrolysis is conducted in a divided cell at a glassy carbon anode at a controlled potential of 1.0 V vs. SCE in 5 ml of anolyte (DMF/water, 8:1, 0.1 M $LiClO_4$) with 1 mmol of **40**, 0.1 mmol of $PdCl_2$, and 0.2 mmol of **23**. Besides **42** as the main product also isomeric octanones are detected, the formation of which is due to the oxidation of isomerized 1-octene. This isomerization is accelerated by the addition of acid. As the anolyte becomes acidic during the electrolysis, the isomerization is enhanced. Efforts to neutralize the acid by the addition of sodium hydrogencarbonate or triethylamine lead to a strong decrease of the current. The isomerization can be suppressed, however, if **40** remains for a shorter time in the electrolyte, which is achieved by the addition of **40** in several portions, and if the $PdCl_2$ concentration is decreased to 0.02 mmol. Under these conditions, **40** is oxidized in 75% yield (85% current yield) to **42**. Side products now can be detected only in traces by GLC. The handling of **41a** is easier than that of **40**. It is less volatile and isomerizes only to the side product **44**. The results obtained with **41a** are summarized in Table 6.

Table 6. Indirect electrolyses of **41a** with $PdCl_2$ and different benzoquinones[a]

Quinone	Yield (%) **43**	Yield (%) **41a** + **44**	Current yield (%)	Mass balance
23	79	8	84	84
1b	77	13	86	90
27b	82	9	82	81

[a] Reaction conditions: 1 mmol of **41a**, 0.02 mmol of $PdCl_2$, 0.2 mmol of quinone, DMF/H_2O 8:1, 0.1 M $LiClO_4$, 1.0 V vs. SCE.

Yields are good with **23** as well as with substituted quinones **1b**, **27b**, which can be bound to a polymer support.

Mechanistic Considerations and Discussion

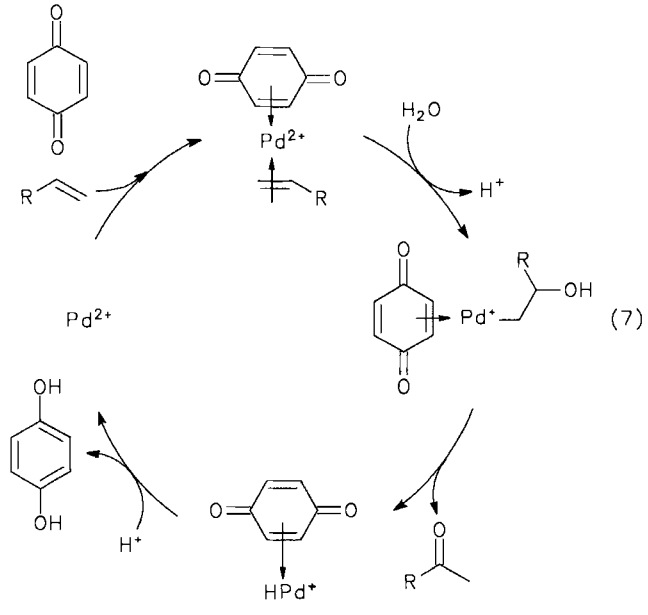
In Figure 4 the yields of the palladium(II)-catalyzed oxidation of the alkenes **40** and **41a** are presented in the order of the reduction potential $E_{p,c}$ of the quinones.

Good yields are obtained with **1b**, **1c**, **23**, **39**, and **45**. These five quinones have a similar reduction potential. Decrease as well as increase of the reduction potential leads to decreased yields and conversions. A steric influence of the aryl substituent is indicated by the decrease in the ketone yield by 10% when comparing **23** with **1b**.

The experimental results can be tentatively explained by assuming the formation of a palladium(II)-quinone complex (eq. 7), whose existence, however, will need further experimental support.

It is supposed that $PdCl_2$ reacts with the alkene and the quinone to form a complex. Nucleophilic attack of water then leads to a σ bond between palladium and the alkene. A coordination of benzoquinone to palladium has been demonstrated in the 1,4-oxidation of cyclohexadiene in the (π-allyl)palladium intermediate[47a]. When the complex decomposes to the ketone, the quinone ligand is either bound to Pd(0) or disproportionates into Pd(II) and hydroquinone. The acid-catalyzed conversion of a Pd(0)-quinone complex to Pd(II) and hydroquinone has been reported recently[47b]. In the following step the hydroquinone is reoxidized at the anode. Electron-attracting substituents on the quinone ring decrease the electron density at the double bond and should disfavor the complex formation with Pd(II). Electron-donating substituents on the quinone on the other hand should slow down the oxidation of the palladium(0) by the quinone.

While our investigation was nearly completed, Wayner[43] described Wacker oxidations of olefins at the anode mediated by benzoquinone, which supplement our results. 1-Decene, styrene, and *trans*-2-octene were converted in acetonitrile/water with 1 mol% of $Pd(OAc)_2$, 20 mol% of benzoquinone, and varying amounts of perchloric acid in 46–76% yield to the corresponding ketones. The presence of acid was important in this case to increase the reaction rate.



(7)

We found that in neutral DMF/water higher yields of ketone are obtained than in neutral acetonitrile/water (Table 4). An acidic medium increases the rate of the olefin oxidation, but it also may be unfavorable, because it can catalyze the isomerization of the olefin. The formation of isomeric octanones could be suppressed in our oxidation by the use of a neutral electrolyte.

Furthermore, our findings demonstrate that the aryl-substituted quinone **1b** and the alkyl-substituted quinone **27b** give the same yields as benzoquinone (**23**) (Table 6). This result is essential if one wants to use a benzoquinone as mediator that is immobilized at the electrode surface by way of these substituents.

The alkenes **41a**, **b** have been used repeatedly as substrates for the palladium(II)-catalyzed oxidation. They are therefore suitable for a comparison of the different palladium(II) regenerations (Table 7).

The regeneration of palladium(II) with quinone, that itself is anodically regenerated, leads to a slightly higher ke-

tone yield than in the regeneration with $CuCl/O_2$. Also quinones bearing an aryl or alkyl group, which are necessary to bind the quinone to a polymeric support, are suitable mediators for the anodic Wacker oxidation.

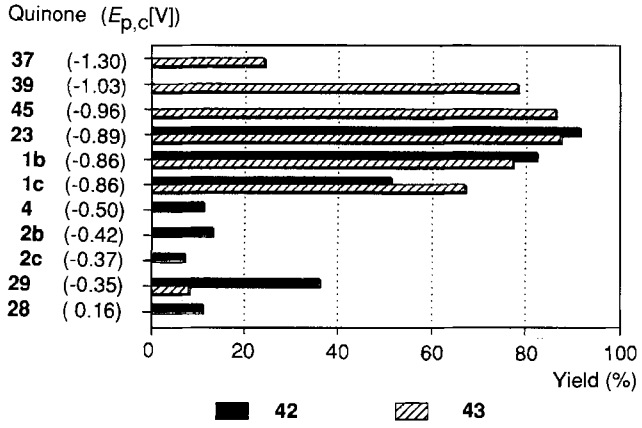


Figure 4. Yield of **42** and **43** in dependence on the cathodic peak potential $E_{p,c}$ of the quinones

Table 7. Comparison of different methods for the Pd(II) regeneration

Alkene	Yield (%) Ketone	Reaction conditions	Ref.
41a	77	0.16 equiv. $PdCl_2$, CuCl, O_2, DMF	[44]
41a	82	0.05 equiv. $PdCl_2$, 0.05 equiv. **46**, 0.15 equiv. **32**, O_2, DMF	[38a]
41b	82	0.04 equiv. $Pd(OAc)_2$, 0.2 equiv. **23**, DMSO, current controlled regeneration	[38b]
41a	87	0.05 equiv. $PdCl_2$, 1.1 equiv. **23**, DMF	this work
41a	82	0.02 equiv. $PdCl_2$, 0.2 equiv. **27b**, DMF potential-controlled regeneration	this work

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Experimental

Melting points (uncorrected): Kofler hot-stage. – IR: Shimadzu IR-408. – ^1H, ^{13}C NMR: Bruker WM 300 and AM 360, TMS for ^1H, $CDCl_3$ or [D_6]acetone for ^{13}C as internal standard. – GC/MS: Varian GC 3400, Finnigan MAT 8230, data system SS 300, 70 eV. – Elementary analyses: Mikroanalytisches Laboratorium M. Beller, Göttingen. – GC: Varian 1400, Spectra Physics Integrator Autolab; Shimadzu GC-9A and GC-14A with integrator C-R3A; glass column: 1.7 m × 2 mm, 10% Carbowax on chromosorb WAW; quartz capillary column 25 m × 0.32 mm, 0.25 µm SE 54; quartz capillary column 25 m × 0.21 mm, 0.25 µm CW 20 M. – HPLC: Knauer HPLC pump 64, differential refractometer 51.78; Knauer column: nucleosil 100-5, 5 µm, 8 mm; Showa Denko K. K.: Shodex AD 802/S and AD 803/S (ethyl acetate). – Cyclic voltammetry: a) Heka potentiostat PG 285 combined with Commodore computer PC-40, b) Jaissle potentiostat IPM 83-100 V combined with IBS microcomputer Space-84, c) Bank potentiostat LB75L combined with Apple IIe. For b), c) the program LUPINE[48], version 2.1 was used. Metrohm cell EA 876 with platinum foil electrodes (1 cm^2). – Reference electrodes: saturated calomel electrode (SCE); Ag/0.1 M $AgNO_3$ in acetonitrile. – Preparative scale electrolysis: a) undivided double-walled beaker-type cell (150 ml), platinum net electrode (12 cm^2); b) undivided double-walled beaker-type cell with reference electrode and Luggin capillary (150 ml), platinum net electrode (12 cm^2); c) divided microelectrolysis cell with reference electrode, G3 glass frit as diaphragm, glassy carbon anode (11 mm^2), platinum foil cathode, anolyte: 5 ml. – Current source: Wenking Fast Rise potentiostat 68FR 0.5 and Heinzinger Galvanostat TNS 300–1500.

Preparation of the Benzoquinones

2-(4-Hydroxyphenyl)-1,4-benzoquinone (**1a**) was obtained according to ref.[13] in 35% yield. – IR (KBr): $\tilde{\nu}$ = 3350 cm^{-1} (OH), 1650 (C=O), 1610, 1590, 1510 (C=C). – ^{13}C NMR ([D_6]acetone): δ = 188.0, 187.5 (C-1, -4), 160.0 (C-10), 145.7 (C-2), 137.9, 136.5 (C-5, -6), 131.7 (C-8), 131.0 (C-3), 124.9 (C-7), 115.9 (C-9).

2-(4-Propionyloxyphenyl)-1,4-benzoquinone (**1b**): To 1.0 g (5.0 mmol) of **1a** and 0.65 g (6.4 mmol) of triethylamine in 20 ml of anhydrous acetone was added slowly with ice cooling 0.6 g (6.5 mmol) of propionyl chloride. After stirring at room temp. overnight, the mixture was hydrolyzed with 100 ml of 0.5 M aqueous HCl, stirred for 1 h, extracted with diethyl ether (3 × 50 ml), and the combined ethereal extracts were dried ($MgSO_4$). After flash chromatography (CH_2Cl_2/EtOH, 50:1) 0.98 g (77%) of **1b** was obtained. M.p. 101°C. – IR (KBr): $\tilde{\nu}$ = 1760 cm^{-1} (C=O, ester), 1650 (C=O, quinone), 1590, 1500 (C=C). – ^{13}C NMR ([D_6]acetone): δ = 188.1, 187.2 (C-1, -4), 172.8 (C-11), 153.1 (C-10), 145.2 (C-2), 137.8, 136.8 (C-5, -6), 133.1 (C-3), 131.3 (C-8), 131.2 (C-7), 122.4 (C-9), 27.8 (CH_2), 9.1 (CH_3). – MS, *m/z* (%): 258 (2) [M^+ + 2H], 256 (5) [M^+], 202 (12), 200 (70). – $C_{15}H_{12}O_4$ (256.3): calcd. C 70.31, H 4.72; found C 70.23, H 4.82.

2-[4-(Benzoyloxy)phenyl]-1,4-benzoquinone (**1c**): 0.97 g (4.8 mmol) of **1a** was treated with 0.84 g (6.0 mmol) of benzoyl chloride, as described in the preparation of **1b**. After treatment with 150 ml of 2 N HCl, the mixture was extracted with ethyl acetate (4 × 100 ml), and the combined extracts were dried ($MgSO_4$). Flash chromatography (CH_2Cl_2) afforded 1.4 g (95%) of **1c**. M.p. 176°C. – IR (KBr): $\tilde{\nu}$ = 1725 cm^{-1} (C=O, ester), 1650 (C=O, quinone), 1590, 1500 (C=C). – ^{13}C NMR ([D_6]acetone): δ = 188.2, 187.2 (C-1, -4), 165.2 (C-11), 153.3 (C-10), 145.6 (C-2), 138.0, 137.0 (C-5, -6), 134.6 (C-15), 133.2 (C-3), 131.7 (C-7), 131.5 (C-8), 130.7 (C-13), 130.2 (C-12), 129.9 (C-14), 122.6 (C-9). – MS, *m/z* (%): 306 (1%) [M^+ + 2H], 304 (1.6) [M^+], 105 (100). – $C_{19}H_{22}O_4$ (304.3): calcd. C 74.99, H 3.98; found C 75.00, H 3.98.

2,5-Dichloro-3,6-dihydroxy-1,4-benzoquinone (**2a**) was prepared according to ref.[12] M.p. 285°C (ref.[12] 283–284°C). The IR spectrum coincided with that reported in ref.[49] – ^{13}C NMR ([D_6]acetone): δ = 165.3 (C=O, COH), 111.6 (CCl). – MS, *m/z* (%): 208/210/212 (57/41/6) [M^+], 180/182/184 (60/31/4) [M^+ – CO].

2,5-Dichloro-3,6-bis(propionyloxy)-1,4-benzoquinone (**2b**): 2.09 g (10 mmol) of **2a** and 2.78 g (30 mmol) of propionyl chloride were suspended in 30 ml of anhydrous acetone. While cooling with ice, 2.3 g (23 mmol) of triethylamine in 20 ml of anhydrous acetone was added dropwise within 30 min. The dark colored reaction mixture was then stirred overnight at room temp. Then after stirring for 1 h with 150 ml of 0.5 M HCl the solution was extracted with diethyl ether (3 × 100 ml). The combined ethereal extracts were washed with a satd. $NaHCO_3$ solution, dried ($MgSO_4$), and the ether was evaporated in a rotary evaporator. Recrystallization of the brown residue from ethyl acetate yielded 1.7 g (53%) of yellow crystalline **2b**. M.p. 144–145°C. – IR (KBr): $\tilde{\nu}$ = 1780 cm^{-1}

(C=O, ester), 1690 (C=O, quinone), 1610 (C=C). – ^{13}C NMR ([D$_6$]acetone): δ = 172.7 (C=O, quinone), 170.7 (C=O, ester), 149.8 (C–O), 131.9 (CCl), 27.3 (CH_2), 8.9 (CH_3). – MS, *m/z* (%): 320/322/324 (0.3/0.3/0.1) [M^+], 57 (100) [$C_3H_5O^+$]. – $C_{12}H_{10}Cl_2O_6$ (321.1): calcd. C 44.89, H 3.14, Cl 22.08; found C 44.86, H 3.14, Cl 22.00.

2,5-Bis(benzoyloxy)-3,6-dichloro-1,4-benzoquinone (**2c**): 1.04 g (5.0 mmol) of **2a**, 2.81 g (20 mmol) of benzoyl chloride, and 1.41 g (14 mmol) of triethylamine in 50 ml of anhydrous acetone were heated under reflux for 6 h. Then 150 ml of 0.5 M HCl was added and the mixture stirred for 2–3 h. After workup as described for **2b**, 1.4 g (67%) of **2c** was obtained. M.p. 217–218°C (ref.[50] 212–214°C). – IR (KBr): $\tilde{\nu}$ = 1750 cm^{-1} (C=O, ester), 1690 (C=O, quinone), 1610 (C=C). – ^{13}C NMR ($CDCl_3$): δ = 171.6 (C-1, -4), 162.3 (COC_6H_5), 149.2, 134.8, 132.3 (C-2, -5), 130.8, 128.9, 126.9 (C-3, -6). – $C_{20}H_{10}Cl_2O_6$ (417.2): calcd. C 57.58, H 2.42, Cl 17.00; found C 57.73, H 2.57, Cl 17.03.

Trichloro-hydroxy-1,4-benzoquinone (**3a**) was prepared according to ref.[11] – IR (KBr): $\tilde{\nu}$ = 3450 cm^{-1} (OH), 1680 (C=O), 1660 (C=C). – ^{13}C NMR ([D$_6$]acetone): δ = 173.6, 172.4 (C=O), 154.0 (COH), 141.4, 137.2 (Cl–C=C–Cl), 115.0 (Cl–*C*=C–OH).

Trichloro-(propionyloxy)-1,4-benzoquinone (**3b**): To 1.1 g (5.0 mmol) of **3a** and 0.61 g (6.0 mmol) of triethylamine in 50 ml of anhydrous acetone was added dropwise 0.74 g (8.0 mmol) of propionyl chloride in 20 ml of anhydrous acetone. After stirring overnight at room temp. and workup of the reaction mixture as described for **1b**, the crude product was subjected to purification by flash chromatography (CH_2Cl_2/EtOH, 10:1). The resulting brown oil (1.04 g, 72%) was still impure, presumably due to decomposition on the column. It could be stored with minor decomposition for 4 d in the refrigerator. – IR (KBr): $\tilde{\nu}$ = 1770 cm^{-1} (C=O, ester), 1680 (C=O, quinone), 1610 (C=C). – ^{13}C NMR ([D$_6$]acetone): δ = 171.5, 170.9 (C=O, quinone), 170.2 (C=O, ester), 149.1 (C–O, quinone), 141.2, 139.2, 132.7 (CCl), 26.9 (CH_2), 8.5 (CH_3).

2-(Phenylsulfonyl)-1,4-benzoquinone (**4**): A solution of 10 g (61 mmol) of sodium benzenesulfinate in 75 ml of water was acidified with 25 ml of dilute HCl. To the solution 6.0 g (56 mmol) of benzoquinone was added in portions to yield a white precipitate. After stirring for 4 h, the precipitate was separated by filtration and washed with water. The product was dissolved in ethanol and precipitated from the solution by the addition of water to yield 11.5 g (83%) of 2-(phenylsulfonyl)hydroquinone (**5**). M.p. 200°C (ref.[51] 196°C). – IR (KBr): $\tilde{\nu}$ = 3300 cm^{-1} (OH), 1370 (SO_2). – ^{1}H NMR ([D$_6$]acetone): δ = 6.85 (d, ^5J = 3 Hz, 1H, 3-H), 7.02 (dd, ^4J = 8.8, ^5J = 3 Hz, 1H, 5-H), 7.36 (d, ^4J = 8.9 Hz, 1H, 6-H), 7.55–7.75 (m, 3H, 9-, 10-H), 8.01 (m, 2H, 8-H). – ^{13}C NMR ([D$_6$]acetone): δ = 150.6 (C-4), 148.8 (C-1), 142.2 (C-7), 133.6 (C-10), 129.3 (C-9), 127.7 (C-8), 125.9 (C-2), 123.7 (C-5), 119.5 (C-6), 114.4 (C-3). – MS, *m/z* (%): 250 (61) [M^+], 186 (7) [$M^+ - SO_2$]. – $C_{12}H_{10}O_4S$ (250.3): calcd. C 57.59, H 4.03; found C 57.52, H 4.03.

2.5 g (10 mmol) of **5**, 4.0 g (14.5 mmol) of silver carbonate, and about 2 g of magnesium sulfate were suspended in 50 ml of toluene, and the suspension was stirred for 2 h at room temp. Subsequently, it was heated to reflux, and precipitated silver was filtered off. After washing of the precipitate with hot toluene, the toluene solution was concentrated to 5 ml, the precipitated yellow solid collected and recrystallized from ethyl acetate to yield 2.02 g (82%) of **4**, that still contained some **5**. An analytical pure sample was obtained by repeated recrystallization from ethyl acetate and toluene. M.p. 137°C. – IR (KBr): $\tilde{\nu}$ = 1660 cm^{-1} (C=O), 1610 (C=C), 1310 (SO_2). – ^{1}H NMR ([D$_6$]acetone): δ = 6.84 (d, ^4J = 10 Hz, 1H, 6-H), 6.97 (dd, ^4J = 10.3, ^5J = 2.4 Hz, 1H, 5-H), 7.54 (d, ^5J = 2.6 Hz, 1H, 3-H), 7.6–7.8 (m, 3H, 9-, 10-H), 8.01 (m, 2H, 8-H). – ^{13}C NMR ([D$_6$]acetone): δ = 186.7, 181.7 (C-1, -4), 145.4 (C-2), 139.7 (C-7), 138.4 (C-3), 137.74, 137.65 (C-5, -6), 135.2 (C-10), 129.93, 129.88 (C-8, -9). – MS, *m/z* (%): 250 (16) [$M^+ - 2H$], 248 (2) [M^+], 184 (20) [$M^+ - SO_2$]. – $C_{12}H_8O_4S$ (248.3): calcd. C 58.06, H 3.25; found C 57.96, H 3.25.

2,3,5-Trimethyl-6-[(propionyloxy)methyl]-1,4-benzoquinone (**6b**)

1,4-Dimethoxy-2,3,5-trimethylbenzene (**10**) was prepared according to ref.[52] in 77% yield from trimethylhydroquinone.

1-Bromo-2,5-dimethoxy-3,4,6-trimethylbenzene (**11**): To a solution of 7.03 g (39.1 mmol) of **10** in 40 ml of dichloromethane a catalytic amount of iron powder and then with ice cooling within 30 min 2.3 ml (45 mmol) of bromine in 20 ml of dichloromethane were added dropwise. After stirring for 2 h at room temp., 150 ml of diethyl ether was added, and the organic layer was subsequently extracted successively with 50 ml of dil. sulfuric acid, dil. sodium hydroxide, dil. sulfuric acid, and water. After drying ($MgSO_4$) of the organic layer and partial evaporation of the diethyl ether, a slightly yellow residue was obtained that was recrystallized from a small volume of methanol to yield 10.0 g (99%) of **11**. M.p. 71–72°C (ref.[53] 71–72°C). – ^{1}H NMR ($CDCl_3$): δ = 2.18, 2.24, 2.36 (s, 9H, 3-, 4-, 6-CH_3), 3.66, 3.75 (s, 6H, OCH_3). – ^{13}C NMR ($CDCl_3$): δ = 12.7, 13.2, 16.5 (q, 3-, 4-, 6-CH_3), 60.1, 60.2 (q, OCH_3), 117.5 (s, C-1), 129.3, 129.4, 129.8 (s, C-3, -6), 151.5, 153.3 (s, C-2, -5). – MS, *m/z* (%): 260/258 (79/83) [M^+], 245/243 (87/100) [$M^+ - CH_3$]. – $C_{11}H_{15}BrO_2$ (259.1): calcd. C 50.98, H 5.83, Br 30.83; found C 51.06, H 5.87, Br 30.94.

2,5-Dimethoxy-3,4,6-trimethylbenzoic Acid (**13**): To 3.90 g (15.1 mmol) of **11** in 20 ml of anhydrous diethyl ether was added under nitrogen at –20°C 7.5 ml of a *n*-butyllithium solution (18.6 mmol, 2.5 M in *n*-hexane). After stirring for 1 h, dry carbon dioxide was bubbled through the solution for 2 h during which time it was warmed up to room temp. Then the mixture was hydrolyzed with 50 ml of water and 20 ml of dil. sodium hydroxide, the aqueous layer was washed with diethyl ether (3 × 50 ml) and then acidified with dil. hydrochloric acid. After extraction with diethyl ether (3 × 100 ml), drying of the combined organic layers ($MgSO_4$), and evaporation of the diethyl ether a white solid was obtained, which was further purified by CC (petroleum ether/diethyl ether/acetic acid, 100:100:1, R_f = 0.39) to yield 2.40 g (71%) of **13**. M.p. 98–101°C (ref.[54] 100–101°C). – IR (KBr): $\tilde{\nu}$ = 1690 cm^{-1} (C=O). – ^{1}H NMR ($CDCl_3$): δ = 2.16, 2.20, 2.32 (s, 9H, 3-, 4-, 6-CH_3), 3.64, 3.76 (s, 6H, OCH_3). – ^{13}C NMR ($CDCl_3$): δ = 12.5, 13.0, 13.1 (3-, 4-, 6-CH_3), 60.1, 62.2 (OCH_3), 125.5, 127.0, 129.0, 133.8 (C-1, -3, -4, -6), 151.4, 153.1 (C-2, -5), 172.7 (CO_2H). – MS, GC/MS as methyl ester, *m/z* (%): 238 (88) [M^+], 223 (30) [$M^+ - CH_3$]. – $C_{12}H_{16}O_4$ (224.2): calcd. C 64.27, H 7.19; found C 64.37, H 7.17.

2,5-Dimethoxy-3,4,6-trimethylbenzyl Alcohol (**14a**): 0.89 g (3.97 mmol) of **13** in 10 ml of anhydrous diethyl ether and 0.39 g (10.3 mmol) of $LiAlH_4$ were stirred overnight, and subsequently the mixture was heated under reflux for complete conversion. After hydrolysis with water and acidification with dil. HCl the aqueous layer was extracted with diethyl ether (3 × 25 ml). After drying of the combined ethereal extracts ($MgSO_4$) and removal of diethyl ether, flash chromatography of the white solid (petroleum ether/diethyl ether, 1.5:1) or recrystallization from petroleum ether afforded 0.78 g (94%) of **14a**. M.p. 120–121°C. – ^{1}H NMR ($CDCl_3$): δ = 2.18, 2.20, 2.32 (s, 9H, 3-, 4-, 6-CH_3), 3.65, 3.74 (s, 6H, OCH_3), 4.73 (s, 2H, CH_2OH). – ^{13}C NMR ($CDCl_3$): δ = 11.6, 12.4, 12.7 (q, 3-, 4-, 6-CH_3), 57.5 (t, CH_2OH), 59.9, 61.5 (q, OCH_3), 128.0, 128.1, 130.0, 130.7 (s, C-1, -3, -4, -6), 153.1, 153.2

(s, C-2, -5). – MS, *m/z* (%): 210 (100) [M^+], 195 (29) [$M^+ - CH_3$]. – $C_{12}H_{18}O_3$ (210.3): calcd. C 68.54, H 8.63; found C 68.51, H 8.76.

1,4-Dimethoxy-2,3,5-trimethyl-6-[(propionyloxy)methyl]benzene (**14b**): 525 mg (2.50 mmol) of **14a** and 300 mg (3.26 mmol) of propionyl chloride was stirred overnight with ice cooling in 5 ml of anhydrous diethyl ether and 400 mg (5.00 mmol) of pyridine. Then 50 ml of water was added, the mixture was acidified with dil. HCl, extracted with diethyl ether (3 × 50 ml), the combined organic layers were dried ($MgSO_4$), and after evaporation of diethyl ether the residue was purified by flash chromatography (petroleum ether/diethyl ether, 3:1) to afford 610 mg (92%) of **14b**. M.p. 62–63°C. – IR (KBr): $\tilde{\nu}$ = 1730 cm^{-1} (C=O). – ^1H NMR ($CDCl_3$): δ = 1.12 (t, ^3J = 7.6 Hz, 3H, CH_3CH_2), 2.16, 2.18, 2.21 (s, 9H, 2-, 3-, 5-CH_3), 2.31 (q, ^3J = 7.6 Hz, 2H, CH_3OCH_2), 3.63, 3.65 (s, 2H, OCH_3), 5.17 (s, 2H, CH_2O). – ^{13}C NMR ($CDCl_3$): δ = 9.0 (CH_3CH_2), 11.7, 12.5, 12.7 (2-, 3-, 5-CH_3), 27.4 (CH_3CH_2), 59.2 (CH_2O), 59.9, 61.7 (OCH_3), 125.1, 128.2, 129.2, 131.9 (C-2, -3, -5, -6), 152.9, 153.8 (C-1, -4), 174.3 ($CH_3CH_2CO_2$). – MS, *m/z* (%): 266 (30) [M^+], 192 (100) [$M^+ - C_2H_5CO_2H$]. – $C_{15}H_{22}O_4$ (266.3): calcd. C 67.64, H 8.33; found C 67.74, H 8.39.

Benzoquinone **6b**: To 660 mg (2.48 mmol) of **14b** in 50 ml of water and 50 ml of benzene was added with intense stirring 13.3 g (30.2 mmol) of silver(II) bis(2,6-dipicolinate)[16] in small portions. After complete conversion (TLC control) the suspension was filtered and the precipitate washed with diethyl ether. After separation of the organic layer the aqueous layer was extracted with diethyl ether (2 × 50 ml), the combined organic layers were dried ($MgSO_4$), the ether was evaporated and the crude product purified by flash chromatography (petroleum ether/diethyl ether, 4:1) to afford 370 mg (63%) of **6b**. – IR (Film): $\tilde{\nu}$ = 1740 cm^{-1} (C=O, ester), 1640 (C=O, quinone). – ^1H NMR ($CDCl_3$): δ = 1.09 (t, ^3J = 7.6 Hz, 3H, CH_3CH_2), 2.00, 2.01, 2.08 (s, 9H, 2-, 3-, 5-CH_3), 2.29 (q, ^3J = 7.6 Hz, 2H, CH_3CH_2), 4.99 (s, 2H, 6-CH_2). – ^{13}C NMR ($CDCl_3$): δ = 8.8 (q, CH_3CH_2), 12.1, 12.2, 12.4 (q, 2-, 3-, 5-CH_3), 27.0 (t, CH_3CH_2), 56.9 (t, 6-CH_2), 136.5, 140.5, 140.8, 144.4 (s, C-2, -3, -5, -6), 173.8 (s, $CH_3CH_2CO_2$), 185.5, 187.1 (s, C-1, -4). – MS, *m/z* (%): 236 (3) [M^+], 180 (94) [$M^+ - C_2H_4CO$]. – $C_{13}H_{16}O_4$ (236.3): calcd. C 66.09, H 6.83; found C 66.14, H 6.87.

2,3,5-Trimethyl-6-[2-(propionyloxy)propyl]-1,4-benzoquinone (**7b**)

1-(2-Hydroxypropyl)-2,5-dimethoxy-3,4,6-trimethylbenzene (**15a**): To 10.2 g (39.3 mmol) of **11** in 50 ml of anhydrous diethyl ether was added under nitrogen at 10°C 20 ml of a *n*-butyllithium solution (2.5 M in hexane, 50 mmol). After stirring for 1 h, 4.2 ml (3.6 g, 62 mmol) of propylene oxide was added, and the mixture was stirred overnight at room temp. For workup the mixture was treated with 50 ml of water, then acidified with dil. HCl, and the aqueous layer was extracted with diethyl ether (3 × 50 ml). The combined ethereal solutions were dried ($MgSO_4$), and most of the ether was evaporated. After the addition of an equal amount of petroleum ether at 0°C, a white solid of 6.93 g (74%) of **15a** crystallized. M.p. 79–80°C. – ^1H NMR ($CDCl_3$): δ = 1.23 (d, ^3J = 6.3 Hz, 3H, CH_3CHCH_2), 2.16, 2.20 (s, 9H, 3-, 4-, 6-CH_3), 2.77 (d, ^3J = 6.1 Hz, 2H, CH_2CHCH_3), 3.61, 3.64 (s, 6H, OCH_3), 3.95 (qt, ^3J = 6.3, 6.1 Hz, 1H, CH_2CHCH_3). – ^{13}C NMR ($CDCl_3$): δ = 12.5, 12.7, 12.8 (3-, 4-, 6-CH_3), 23.5 (CH_3CHCH_2), 36.8 (CH_2CHCH_3), 60.0, 60.2 (OCH_3), 68.5 (CH_2CHCH_3), 127.78, 127.84, 128.4, 129.1 (C-1, -3, -4, -6), 153.0, 153.2 (C-2, -5). – MS, *m/z* (%): 238 (28) [M^+], 220 (6) [$M^+ - H_2O$], 194 (66), 179 (100). – $C_{14}H_{22}O_3$ (238.3): calcd. C 70.55, H 9.31; found C 70.70, H 9.42.

1,4-Dimethoxy-2,3,5-trimethyl-6-[2-(propionyloxy)propyl]-benzene (**15b**): 1.01 g (4.2 mmol) of **15a** was treated, as described for **14a**, with 0.55 g (6.0 mmol) of propionyl chloride in 0.79 g (10 mmol) of pyridine and 10 ml of diethyl ether. After workup, as described for **14a**, and flash chromatography (petroleum ether/diethyl ether, 5:1), 1.08 g (87%) of **15b** was obtained. – IR (KBr): $\tilde{\nu}$ = 1730 cm^{-1} (C=O). – ^1H NMR ($CDCl_3$): δ = 1.05 (t, ^3J = 7.6 Hz, 3H, CH_3CH_2), 1.19 (d, ^3J = 6.3 Hz, 3H, CH_3CHCH_2), 2.14, 2.15, 2.25 (s, 9H, 2-, 3-, 5-CH_3), 2.0–2.5 (tm, ^3J = 7.6 Hz, 2H, CH_3CH_2), 2.75–2.95 (AB system, δ_A = 2.90, δ_B = 2.82, $^3J_{AB}$ = 13.3, ^3J_A = 7.0, ^3J_B = 7.1 Hz, 2H, $CH_3CHCH_AH_B$), 3.60, 3.64 (s, 6H, OCH_3), 5.01 (ddq, ^3J = 7.1, 7.0, 6.3 Hz, 1H, CH_2CHCH_3). – ^{13}C NMR ($CDCl_3$): δ = 9.9 (q, CH_3CH_2), 12.6, 12.8 (q, 2-, 3-, 5-CH_3), 19.6 (q, CH_3CHCH_2), 27.7 (t, CH_3CH_2), 33.3 (t, CH_3CHCH_2), 59.8, 60.4 (q, OCH_3), 70.8 (d, CH_3CHCH_2), 127.4, 127.7, 128.0, 129.0 (s, C-2, -3, -5, -6), 152.9, 153.4 (s, C-1, -4), 173.8 (s, $CH_3CH_2CO_2$). – MS, *m/z* (%): 294 (22) [M^+], 237 (3) [$M^+ - C_2H_5CO$], 220 (100). – $C_{17}H_{26}O_4$ (294.4): calcd. C 69.36, H 8.90; found C 69.41, H 8.96.

Benzoquinone **7b**: 740 mg (2.52 mmol) of **15b** was oxidized, as described for **14b**, with 9.6 g (22 mmol) of silver(II) bis(2,6-dipicolinate). After flash chromatography (petroleum ether/diethyl ether, 5:1), 500 mg (75%) of **7b** was obtained. – IR (KBr): $\tilde{\nu}$ = 1730 cm^{-1} (C=O, ester), 1640 (C=O, quinone). – ^1H NMR ($CDCl_3$): δ = 1.02 (t, ^3J = 7.6 Hz, 3H, CH_3CH_2), 1.23 (d, ^3J = 6.2 Hz, 3H, CH_3CHCH_2), 1.97, 2.03 (s, 9H, 2-, 3-, 5-CH_3), 2.08–2.30 (AB system, δ_A = 2.20, δ_B = 2.17, $^3J_{AB}$ = 16.3, ^3J_A = ^3J_B = 7.6 Hz, 2H, $CH_3CH_AH_B$), 2.62–2.83 (AB-system, δ_A = 2.79, δ_B = 2.67, $^3J_{AB}$ = 13.1, ^3J_A = 4.6, ^3J_B = 8.4 Hz, 2H, $CH_3CHCH_AH_B$), 5.01 (ddq, ^3J = 8.4, 7.6, 4.6 Hz, 1H, CH_2CHCH_3). – ^{13}C NMR ($CDCl_3$): δ = 8.7 (q, CH_3CH_2), 12.0, 12.4 (q, 2-, 3-, 5-CH_3), 20.2 (q, CH_3CHCH_2), 27.4 (t, CH_3CH_2), 32.8 (CH_3CHCH_2), 69.6 (t, CH_3CHCH_2), 139.8, 140.19, 140.23, 141.8 (s, C-2, -3, -5, -6), 173.5 (s, $CH_3CH_2CO_2$), 186.4, 187.1 (s, C-1, -4). – MS, *m/z* (%): 220 (6) [$M^+ - C_2H_4O$], 208 (12) [$M^+ - C_2H_4CO$]. – $C_{15}H_{20}O_4$ (264.3): calcd. C 68.16, H 7.63; found C 68.26, H 7.73.

2,3,5-Trimethyl-6-[3-(propionyloxy)propyl]-1,4-benzoquinone (**8b**)

1-(3-Hydroxypropyl)-2,5-dimethoxy-3,4,6-trimethylbenzene (**17a**): To 5.20 g (20.0 mmol) of **11** in 50 ml of anhydrous diethyl ether was added under nitrogen at –15°C dropwise 10 ml of a *n*-butyllithium solution (2.5 M in *n*-hexane, 25 mmol). After stirring for 2 h, 4.80 g (25.2 mmol) of copper(I) iodide in 7 ml of dimethyl sulfide was added to the mixture. After 3 h 3.60 g (29.8 mmol) of allyl bromide was slowly added, and the mixture was warmed up to room temp. overnight. After hydrolysis with 2 ml of water the ethereal solution was separated, dried ($MgSO_4$) and the ether evaporated. After filtration of the residue over silica gel (diethyl ether) the obtained crude **16** was dissolved in 50 ml of anhydrous diethyl ether. To the obtained solution was added under nitrogen at 0°C 10 ml of a diborane solution (10 mmol, 1 M in THF). After stirring overnight with ice cooling, a mixture of 20 ml of a 30% hydrogen peroxide solution and 40 ml of dil. sodium hydroxide was slowly added. The mixture was stirred for 2 h, subsequently 50 ml of water was added, and then the mixture was extracted with diethyl ether (4 × 50 ml). After CC (petroleum ether/diethyl ether, 1:1), 2.80 g (59%) of **17a** was obtained as a white solid. M.p. 40–41°C. – ^1H NMR ($CDCl_3$): δ = 1.68 (tt, ^3J = 7.0, 5.8 Hz, 2H, $CH_2CH_2CH_2OH$), 2.11, 2.15 (s, 9H, 3-, 4-, 6-CH_3), 2.68 (t, ^3J = 7.0 Hz, 2H, $CH_2CH_2CH_2OH$), 3.43 (t, ^3J = 5.8 Hz, 2H, $CH_2CH_2CH_2OH$), 3.57, 3.81 (s, 6H, OCH_3). – ^{13}C NMR ($CDCl_3$): δ = 11.8, 12.6, 12.8 (q, 3-, 4-, 6-CH_3), 22.6 (t, $CH_2CH_2CH_2OH$), 32.0 (t, $CH_2CH_2CH_2OH$), 59.9, 60.9 (q, OCH_3), 61.2 (t, $CH_2CH_2CH_2OH$), 127.3, 127.5, 128.4, 130.6 (s, C-1, -3, -4, -6), 152.8, 153.3 (s, C-2, -5). – MS, *m/z* (%): 238 (100) [M^+], 223 (8) [$M^+ - CH_3$], 220 (5)

[$M^+ - H_2O$]. – $C_{14}H_{22}O_3$ (238.3): calcd. C 70.55, H 9.30; found C 70.50, H 9.44.

An analytical pure sample of *1,4-dimethoxy-2,3,5-trimethyl-6-(prop-2-enyl)benzene* (**16**) was obtained by flash chromatography (petroleum ether). – ^{1}H NMR ($CDCl_3$): δ = 2.17 (s, 9H, 2-, 3-, 5-CH_3), 3.41 (ddd, ^3J = 5.6, ^4J = 1.8, 1.8 Hz, 2H, CH_2CH=CH_2), 3.62, 3.64 (s, 6H, OCH_3), 4.88 (ddt, $^3J_{trans}$ = 17.1, $^2J_{gem}$ = 1.8, ^4J = 1.8 Hz, 1H, CH_2CH=CH_2), 4.98 (ddt, $^3J_{cis}$ = 10.2, $^2J_{gem}$ = 1.8, ^4J = 1.8 Hz, 1H, CH_2CH=CH_2), 5.92 (ddt, $^3J_{trans}$ = 17.1, $^3J_{cis}$ = 10.2, ^3J = 5.6 Hz, 1H, CH_2CH=CH_2). – ^{13}C NMR ($CDCl_3$): δ = 11.8, 12.5, 12.6 (q, 2-, 3-, 5-CH_3), 31.1 (t, CH_2CH=CH_2), 59.8, 60.8 (q, OCH_3), 114.6 (t, CH_2CH=CH_2), 127.7, 127.8, 128.5, 129.0 (s, C-2, -3, -5, -6), 152.8, 152.9 (s, C-1, -4). – MS, *m/z* (%): 220 (100) [M^+], 205 (62) [$M^+ - CH_3$], 190 (42) [$M^+ - CH_2O$]. – $C_{14}H_{20}O_2$ (220.2): calcd. C 76.33, H 9.15; found C 76.44, H 8.98.

2-(Hydroxymethyl)-3,5,6-trimethyl-1,4-benzoquinone (**6a**)

1-[(tert-Butyldimethylsilyloxy)methyl]-2,5-dimethoxy-3,4,6-trimethylbenzene (**14c**): 2.73 g (13.0 mmol) of **14a**, 1.11 g (16.0 mmol) of imidazole, 2.30 g (15.0 mmol) of *tert*-butyldimethylsilyl chloride, and a catalytic amount of 4-(dimethylamino)pyridine in 15 ml of anhydrous DMF were stirred at room temp. overnight. To this mixture was then added 50 ml of water, followed by extraction with diethyl ether (4 × 50 ml), drying of the combined ethereal extracts ($MgSO_4$), evaporation of the ether, and flash chromatography of the residue (petroleum ether). Yield of **14c** 3.69 g (87%), m.p. 58–61°C. – ^{1}H NMR ($CDCl_3$): δ = 0.11 [s, 6H, $Si(CH_3)_2$], 0.90 [s, 9H, $SiC(CH_3)_3$], 2.16, 2.17, 2.3 (s, 9H, 3-, 4-, 6-CH_3), 3.6, 3.7 (s, 6H, OCH_3), 4.70 (s, 2H, 1-CH_2). – ^{13}C NMR ($CDCl_3$): δ = −5.4 [q, $Si(CH_3)_2$], 11.8, 12.5, 12.8 (q, 3-, 4-, 6-CH_3), 18.4 [s, Si$C(CH_3)_3$], 25.9 [q, $SiC(CH_3)_3$], 57.5 (t, 1-CH_2), 60.0, 62.0 (q, OCH_3), 127.9, 129.1, 130.0, 130.5 (s, C-1, -3, -4, -6), 153.0 (s, C-2, -5). – MS, *m/z* (%): 324 (2) [M^+], 267 (76) [$M^+ - C(CH_3)_3$], 252 (100) [$M^+ - C(CH_3)_3 - CH_3$]. – $C_{18}H_{32}O_3Si$ (324.5): calcd. C 66.62, H 9.94; found C 66.56, H 10.14.

1-[(tert-Butyldimethylsilyloxy)methyl]-3,3,6,6-tetramethoxy-2,4,5-trimethyl-1,4-cyclohexadiene (**18**): 2.99 g (9.23 mmol) of **14c** was oxidized in an undivided, double-walled cell at controlled current (1 A) in 1.0 g of potassium hydroxide and 100 ml of methanol as the electrolyte at a platinum gauze anode (12 cm^2) and a platinum foil cathode (1 cm^2) at 0°C. The progress of the reaction was followed by TLC. After total conversion of **14c**, the electrolyte was concentrated by vacuum distillation, then 50 ml of water was added to the residue which was extracted with diethyl ether (4 × 50 ml). The combined organic layers were dried ($MgSO_4$), and the ether was evaporated. The residue was recrystallized from a small volume of petroleum ether to afford 2.37 g (67%) of **18**. M.p. 123–125°C. – ^{1}H NMR ($CDCl_3$): δ = 0.08 [s, 6H, $Si(CH_3)_2$], 0.87 [s, 9H, $SiC(CH_3)_3$], 1.69, 1.71 (q, ^5J = 0.8 Hz, 6H, 4-, 5-CH_3), 1.84 (s, 3H, 2-CH_3), 2.99, 3.00 (s, 12H, OCH_3), 4.19 (s, 2H, CH_2O). – ^{13}C NMR ($CDCl_3$): δ = −6.0 [q, $Si(CH_3)_2$], 10.9, 11.0, 11.2 (q, 2-, 4-, 5-CH_3), 17.9 [s, Si$C(CH_3)_3$], 25.5 [q, $SiC(CH_3)_3$], 50.8, 51.3 (q, OCH_3), 56.1 (t, CH_2O), 98.2, 98.6 (s, C-3, -6), 135.3, 135.5, 138.1, 140.9 (s, C-1, -2, -4, -5). – MS, *m/z* (%): 329 (5) [$M^+ - C(CH_3)_3$], 299 (22) [$M^+ - C(CH_3)_3 - CH_2O$]. – $C_{20}H_{38}O_5Si$ (386.6): calcd. C 62.13, H 9.91; found C 61.95, H 9.92.

Benzoquinone **6a**: 1.02 g (2.64 mmol) of **18** in 25 ml of acetone was stirred with 5 ml of dil. HCl at room temp. for 4 h. Subsequently, 100 ml of water was added to the mixture which was extracted with diethyl ether (4 × 100 ml). The combined ethereal extracts were dried ($MgSO_4$), the ether was evaporated and the residue purified by flash chromatography (petroleum ether/diethyl ether, 1:1) to afford 460 mg (97%) of **6a**. M.p. 79°C. – IR (KBr): $\tilde{\nu}$ = 3400 cm^{-1} (OH), 1650 (C=O). – ^{1}H NMR ($CDCl_3$, D_2O exchange): δ = 2.00, 2.01 (q, ^5J = 1.2 Hz, 6H, 5-, 6-CH_3), 2.07 (s, 3H, 3-CH_3), 4.53 (s, 2H, CH_2OH). – ^{13}C NMR ($CDCl_3$): δ = 11.7, 12.0, 12.4 (q, 3-, 5-, 6-CH_3), 57.6 (t, CH_2OH), 140.1, 140.5, 141.3, 141.5 (s, C-2, -3, -5, -6), 187.6, 188.4 (s, C-1, -4). – MS, *m/z* (%): 180 (100) [M^+], 152 (28) [$M^+ - CO$]. – $C_{10}H_{12}O_3$ (180.2): calcd. C 66.65, H 6.71; found C 66.62, H 6.93.

2-(2-Hydroxypropyl)-3,5,6-trimethyl-1,4-benzoquinone (**7a**)

1-[2-(tert-Butyldimethylsilyloxy)propyl]-2,5-dimethoxy-3,4,6-trimethylbenzene (**15c**): 4.16 g (17.5 mmol) of **15a**, 1.80 g (26.5 mmol) of imidazole, and 3.60 g (23.9 mmol) of *tert*-butyldimethylsilyl chloride were allowed to react, as described for **14a**, to furnish 5.64 g (91%) of **15c**. – ^{1}H NMR ($CDCl_3$): δ = −0.89, −0.19 [s, 6H, $Si(CH_3)_2$], 0.80 [s, 9H, $SiC(CH_3)_3$], 1.11 (d, ^3J = 6.1 Hz, 3H, CH_3CHOH), 2.14, 2.15, 2.25 (s, 9H, 3-, 4-, 6-CH_3), 2.40–2.90 (AB system, δ_A = 2.77, δ_B = 2.67, $^2J_{AB}$ = 13.1, ^3J_A = 7.1, ^3J_B = 6.5 Hz, 2H, C$H_A H_B$CHOH), 3.61, 3.62 (s, 6H, OCH_3), 4.06 (ddt, ^3J = 7.1, 6.5, 6.1 Hz, 1H, CH_3CHOH). – ^{13}C NMR ($CDCl_3$): δ = −5.1 [q, $Si(CH_3)_2$], 12.7, 12.8, 13.0 (q, 3-, 4-, 6-CH_3), 18.0 [s, Si$C(CH_3)_3$], 23.9 (q, CH_3CHOH), 25.8 [q, $SiC(CH_3)_3$], 37.4 (t, CH_2CHOH), 59.9, 60.2 (q, OCH_3), 69.2 (t, CH_3CHOH), 127.6, 128.2, 128.4, 129.3 (s, C-1, -3, -4, -6), 153.0, 153.5 (s, C-2, -5). – MS, *m/z* (%): 295 (100) [$M^+ - C(CH_3)_3$], 280 (46), 207 (54). – $C_{20}H_{36}O_3Si$ (352.6): calcd. C 68.13, H 10.29; found C 68.06, H 10.54.

1-[2-(tert-Butyldimethylsilyloxy)propyl]-3,3,6,6-tetramethoxy-2,4,5-trimethyl-1,4-cyclohexadiene (**19**): 6.47 g (18.4 mmol) of **15c** was electrolyzed, as described for **14c**, until 17340 Faraday were consumed. Workup afforded 5.10 g (67%) of **19**. M.p. 100–101°C. – ^{1}H NMR ($CDCl_3$): δ = 0.05, 0.08 [s, 6H, $Si(CH_3)_2$], 0.88 [s, 9H, $SiC(CH_3)_3$], 1.19 (d, ^3J = 6.8 Hz, 3H, CH_3CHCH$_2$), 1.70, 1.71, 1.80 (s, 9H, 2-, 4-, 5-CH_3), 2.25–2.55 (AB system, δ_A = 2.47, δ_B = 2.31, $^2J_{AB}$ = 13.2, ^3J_A = 5.8, ^3J_B = 8.0 Hz, 2H, CH_3CHC$H_A H_B$), 2.96, 2.97, 2.98 (s, 12H, OCH_3), 4.21 (dqd, ^3J = 8.0, 6.8, 5.8 Hz, 1H, CH_3CHCH$_2$). – ^{13}C NMR ($CDCl_3$): δ = −4.53, −4.34 [q, $Si(CH_3)_2$], 11.3, 11.5, 12.5 (q, 2-, 4-, 5-CH_3), 18.0 [s, Si$C(CH_3)_3$], 24.4 (q, CH_3CHCH$_2$), 25.9 [q, $SiC(CH_3)_3$], 37.1 (t, CH_3CHCH$_2$), 50.86, 50.89, 50.94 (q, OCH_3), 68.6 (d, CH_3CHCH$_2$), 98.5, 99.2 (s, C-3, -6), 135.65, 135.68, 136.5, 138.8 (s, C-1, -2, -4, -5). – MS, *m/z* (%): 357 (4) [$M^+ - C(CH_3)_3$], 295 (2), 224 (9). – $C_{22}H_{42}O_5Si$ (414.6): calcd. C 63.72, H 10.21; found C 63.88, H 10.45.

Benzoquinone **7a**: 5.10 g (12.3 mmol) of **19** was hydrolyzed, as described for **18**, to afford 2.24 g (88%) of **7a**. M.p. 48–50°C. – IR (KBr): $\tilde{\nu}$ = 3450 cm^{-1} (OH), 1630 (C=O). – ^{1}H NMR ($CDCl_3$): δ = 1.26 (d, ^3J = 6.2 Hz, 3H, CH_3CH), 1.99, 2.04 (s, 9H, 3-, 5-, 6-CH_3), 2.55–2.75 (AB system, δ_A = 2.66, δ_B = 2.64, $^2J_{AB}$ = 12.9, ^3J_A = 5.4, ^3J_B = 7.6 Hz, 2H, C$H_A H_B$CH), 3.91 (dtd, ^3J = 7.6, 6.2, 5.4 Hz, 1H, CHCH$_3$). – ^{13}C NMR ($CDCl_3$): δ = 12.0, 12.1, 12.5 (q, 3-, 5-, 6-CH_3), 23.5 (q, CHCH_3), 36.1 (t, CH_2), 67.2 (d, CHCH$_3$), 140.1, 140.5, 140.8, 141.9 (s, C-2, -3, -5, -6), 187.2, 187.7 (s, C-1, -4). – MS, *m/z* (%): 208 (9) [M^+], 193 (3) [$M^+ - CH_3$], 175 (2), 165 (26). – $C_{12}H_{16}O_3$ (208.2): calcd. C 69.21, H 7.74; found C 69.23, H 7.59.

2-(3-Hydroxypropyl)-3,5,6-trimethyl-1,4-benzoquinone (**8a**)

1-[3-(tert-Butyldimethylsilyloxy)propyl]-2,5-dimethoxy-3,4,6-trimethylbenzene (**17c**): 5.26 g (22.1 mmol) of **17a** was treated, as described for **14a**, with 2.00 g (29.4 mmol) of imidazole and 3.60 g (26.6 mmol) of *tert*-butyldimethylsilyl chloride to afford 7.47 g (96%) of **17c**. – ^{1}H NMR ($CDCl_3$): δ = 0.06 [s, 6H, $Si(CH_3)_2$], 0.90 [s, 9H, $SiC(CH_3)_3$], 1.68 (m, XX′ part of AA′XX′ system, $^3J_{AX} + {}^3J_{A'X}$ = 16.4, ^3J = 6.3 Hz, 2H, CH_2CH_2CHOH), 2.16, 2.21, 2.25 (s, 9H, 3-, 4-, 6-CH_3), 2.65 (m, AA′ part of AA′XX′

system, $^3J_{AX} + {}^3J_{A'X} = 16.4$ Hz, 2H, $CH_2CH_2CH_2OH$), 3.61, 3.65 (s, 6H, OCH_3), 3.68 (t, $^3J = 6.3$ Hz, 2H, $CH_2CH_2CH_2OH$). – ^{13}C NMR ($CDCl_3$): δ = −5.4 [q, $Si(CH_3)_2$], 11.8, 12.5, 12.6 (q, 3-, 4-, 6-CH_3), 18.2 [s, $SiC(CH_3)_3$], 23.8 (t, $CH_2CH_2CH_2OH$), 25.8 [q, $SiC(CH_3)_3$], 33.4 (t, $CH_2CH_2CH_2OH$), 59.7, 60.6 (q, OCH_3), 63.0 (t, CH_2CH_2OH), 127.1, 127.6, 127.8, 132.0 (s, C-1, -3, -4, -6), 152.8, 153.0 (s, C-2, -5). – MS, *m/z* (%): 352 (5) [M^+], 295 (77) [$M^+ - C(CH_3)_3$], 280 (100). – $C_{20}H_{36}O_3Si$ (352.6): calcd. C 68.13, H 10.29; found C 67.87, H 10.42.

1-[3-(tert-Butyldimethylsilyloxy)propyl]-3,3,6,6-tetramethoxy-2,4,5-trimethyl-1,4-cyclohexadiene (**20**): 6.46 g (18.4 mmol) of **17c** was electrolyzed, as described for **14c**, until 19684 Faraday were consumed. Work-up afforded 5.45 g (72%) of **20**. M.p. 80–84°C. – ^1H NMR ($CDCl_3$): δ = 0.04 [s, 6H, $Si(CH_3)_2$], 0.88 [s, 9H, $SiC(CH_3)_3$], 1.55–1.80 (m, XX′ part of AA′XX′ system, $^3J_{AX} + {}^3J_{AX'} = 16.9$, $^3J = 6.4$ Hz, 2H, $CH_2CH_2CH_2O$), 1.67, 1.74 (s, 9H, 2-, 4-, 5-CH_3), 2.22 (m, AA′ part of AA′XX′ system, $^3J_{AX} + {}^3J_{A'X} = 16.9$ Hz, 2H, $CH_2CH_2CH_2O$), 2.96 (s, 12H, OCH_3), 3.62 (t, $J = 6.4$ Hz, 2H, $CH_2CH_2CH_2O$). – ^{13}C NMR ($CDCl_3$): δ = −5.7 [q, $Si(CH_3)_2$], 10.8, 10.98, 11.01 (q, 2-, 4-, 5-CH_3), 17.9 [s, $SiC(CH_3)_3$], 22.5 (t, $CH_2CH_2CH_2O$), 25.6 [q, $SiC(CH_3)_3$], 31.6 (t, $CH_2CH_2CH_2O$), 50.6, 50.8 (q, OCH_3), 63.1 (t, $CH_2CH_2CH_2O$), 98.2, 98.8 (s, C-3, -6), 135.3, 135.5, 136.0, 139.3 (s, C-1, -2, -4, -5). – MS, *m/z* (%): 383 (8) [$M^+ - OCH_3$], 357 (27) [$M^+ - C(CH_3)_3$], 295 (20). – $C_{22}H_{42}O_5Si$ (414.6): calcd. C 63.72, H 10.21; found C 63.85, H 10.24.

Benzoquinone **8a**: 2.27 g (5.48 mmol) of **20** was hydrolyzed, as described for **18**, to afford 1.13 g (99%) of **8a**. M.p. 42°C (ref.[20] 42–43°C). – IR (KBr): $\tilde{\nu}$ = 3450 cm^{-1} (OH), 1630 (C=O). – ^1H NMR ($CDCl_3$)[20]: δ = 1.66 (tt, $^3J = 7.4$, 6.1 Hz, 2H, $CH_2CH_2CH_2OH$), 1.99, 2.01 (s, 9H, 3-, 5-, 6-CH_3), 2.56 (t, $^3J = 7.4$ Hz, 2H, $CH_2CH_2CH_2OH$), 3.55 (t, $^3J = 6.1$ Hz, 2H, $CH_2CH_2CH_2OH$). – ^{13}C NMR ($CDCl_3$): δ = 11.7, 12.0, 12.1 (q, 3-, 5-, 6-CH_3), 22.4 (t, $CH_2CH_2CH_2OH$), 31.1 (t, $CH_2CH_2CH_2OH$), 61.4 (t, $CH_2CH_2CH_2OH$), 140.1, 140.3, 140.5, 143.4 (s, C-2, -3, -5, -6), 187.2 (s, C-1, -4). – MS, *m/z* (%): 208 (100) [M^+], 193 (14) [$M^+ - CH_3$], 190 (13), 180 (23), 175 (51).

2-(3-Hydroxypropyl)-1,4-benzoquinone (**27a**)

Allyl tert-Butyldimethylsilyl Ether (**21**): To a solution of 11.6 g (200 mmol) of allyl alcohol, 33.0 g (220 mmol) of *tert*-butyldimethylsilyl chloride, and a catalytic amount of 4-(dimethylamino)pyridine in 100 ml of anhydrous dichloromethane was added dropwise 26 g of triethylamine in 20 ml of dichloromethane. The mixture was then stirred overnight. Subsequently 50 ml of dil. HCl was added, the organic layer separated, and the aqueous layer extracted with 50 ml of diethyl ether. The combined organic layers were dried ($MgSO_4$), concentrated, and the residue was filtered over silica gel. Distillation at 101–102°C/150 Torr afforded 30.6 g (89%) of **21**. $n_D^{20} = 1.4178$. – ^1H NMR ($CDCl_3$): δ = 0.06 [s, 6H, $Si(CH_3)_2$], 0.89 [s, 9H, $SiC(CH_3)_3$], 4.15 (ddd, $^3J = 4.5$, $^4J = 1.9$, 1.8 Hz, 2H, $CH_2{=}CHCH_2$), 5.06 (ddt, $^3J_{cis} = 10.4$, $^2J_{gem} = 1.8$, $^4J = 1.8$ Hz, 1H, $CH_2{=}CHCH_2$), 5.25 (ddt, $^3J_{trans} = 17.2$, $^2J_{gem} = 1.8$, $^4J = 1.9$ Hz, 1H, $CH_2{=}CHCH_2$), 5.9 (ddt, $^3J_{trans} = 17.2$, $^3J_{cis} = 10.4$, $^3J = 4.5$ Hz, 1H, $CH_2{=}CHCH_2$). – ^{13}C NMR ($CDCl_3$): δ = −5.3 [q, $Si(CH_3)_2$], 18.4 [s, $SiC(CH_3)_3$], 25.9 [q, $SiC(CH_3)_3$], 64.0 (t, $CH_2{=}CH{-}CH_2$), 113.8 (t, $CH_2{=}CHCH_2$), 137.5 (d, $CH_2{=}CHCH_2$). – MS, *m/z* (%): 172 (2) [M^+], 157 (2), 115 (100) [$M^+ - C(CH_3)_3$]. – $C_9H_{20}OSi$ (172.3): calcd. C 62.72, H 11.70; found C 62.78, H 11.63.

2-[3-(tert-Butyldimethylsilyloxy)propyl]hydroquinone (**24a**) *and 2-[2-(tert-Butyldimethylsilyloxy)propyl]hydroquinone* (**24b**): 3.44 g (20.0 mmol) of **21** in 20 ml of anhydrous THF was stirred at room temp. under nitrogen with 6.0 ml of a diborane solution (6.0 mmol, 1 M in THF) for 5 h. Subsequently, 0.54 g (5.0 mmol) of **23** was added in portions, and the solution was stirred overnight. For workup the mixture was stirred with 20 ml of a saturated potassium carbonate solution for 30 min, then dil. HCl was added, and the mixture was extracted with diethyl ether (5 × 50 ml). Purification of the crude product by flash chromatography (petroleum ether/diethyl ether, 2.5:1) afforded a mixture of **24a** and **24b** in a ratio of 6:1 (determined by GC integration). The mixture was converted without further purification into **25** and **26**. Analytical pure samples of **24a, b** were obtained by reduction of the pure quinones **25** and **26** with an alkaline sodium dithionite solution and subsequent purification by CC.

24a: ^1H NMR ($CDCl_3$): δ = 0.04 [s, 6H, $Si(CH_3)_2$], 0.90 [s, 9H, $SiC(CH_3)_3$], 1.79, 2.63 (AA′XX′ system, $^3J_{AX} + {}^3J_{AX'} = 15.6$, $^3J = 6.4$ Hz, 4H, $CH_2CH_2CH_2O$), 3.64 (t, $^3J = 6.4$ Hz, 2H, $CH_2CH_2CH_2O$), 6.80 (dd, $^3J = 8.7$, $^4J = 3.1$ Hz, 1H, 5-H), 8.84 (d, $^4J = 3.1$ Hz, 1H, 3-H), 6.96 (d, $^3J = 8.7$ Hz, 1H, 6-H). – ^{13}C NMR ([D_6]acetone): δ = −6.0 [q, $Si(CH_3)_2$], 17.9 [s, $SiC(CH_3)_3$], 25.4 [q, $SiC(CH_3)_3$], 26.3 (t, $CH_2CH_2CH_2O$), 32.8 (t, $CH_2CH_2CH_2O$), 62.2 (t, $CH_2CH_2CH_2O$), 113.0, 115.7, 116.6 (d, C-3, -5, -6), 129.0 (s, C-2), 147.9, 150.1 (s, C-1, -4). – MS, GC/MS as bistrimethylsilyl ether, *m/z* (%): 369 (17) [$M^+ - C(CH_3)_3$], 281 (26), 263 (4). – $C_{15}H_{26}O_3Si$ (282.4): calcd. C 63.79, H 9.28; found C 63.70, H 9.30.

24b: ^1H NMR ($CDCl_3$): δ = −0.09, −0.08 [s, 6H, $Si(CH_3)_2$], 0.86 [s, 9H, $SiC(CH_3)_3$], 1.23 (d, $^3J = 7.2$ Hz, 3H, CH_3CHCH_2), 3.13 (dqd, $^3J = 8.3$, 7.2, 3.1, 1H, CH_3CHCH_2), 3.52–3.93 (AB system, $\delta_A = 3.90$, $\delta_B = 3.57$, $^2J_{AB} = 9.3$, $^3J_A = 3.1$, $^3J_B = 8.3$ Hz, 2H, $CH_3CHCH_AH_B$), 6.53–6.78 (ABX system, $\delta_A = 6.56$, $\delta_B = 6.57$, $\delta_X = 6.75$, $^3J_{BX} + {}^5J_{AX} = 9.1$, $^4J_{AB} = 2.9$ Hz, 3H, 3-, 5-, 6-H). – ^{13}C NMR ($CDCl_3$): δ = −5.8 [q, $Si(CH_3)_2$], 15.3 (q, CH_3CHCH_2), 18.3 [s, $SiC(CH_3)_3$], 25.7 [q, $SiC(CH_3)_3$], 37.4 (d, CH_3CHCH_2), 70.8 (t, CH_3CHCH_2), 114.2, 114.3, 118.0 (d, C-3, 5, -6), 132.3 (s, C-2), 148.9, 149.3 (s, C-1, -4). – MS; GC/MS as bistrimethylsilyl ether, *m/z* (%): 369 (100) [$M^+ - C(CH_3)_3$), 281 (86), 263 (14). – $C_{15}H_{26}O_3Si$ (282.4): calcd. C 63.79, H 9.28; found C 63.61, H 9.24.

2-[3-(tert-Butyldimethylsilyloxy)propyl]-1,4-benzoquinone (**25**) *and 2-[2-(tert-Butyldimethylsilyloxy)propyl]-1,4-benzoquinone* (**26**): A mixture of **24a, b** (see above) was stirred with 2.10 g (7.6 mmol) of silver carbonate and 1.0 g of magnesium sulfate in 50 ml of diethyl ether for 3 h. After filtration, the ether was evaporated from the yellow solution. Flash chromatography of the crude product (petroleum ether/diethyl ether, 18:1) afforded 72.4 mg (62%) of **25** and 160 mg (11%) of **26**.

25: m.p. 37°C. – IR (KBr): $\tilde{\nu}$ = 1650 cm^{-1} (C=O). – ^1H NMR ($CDCl_3$): δ = 0.02 [s, 6H, $Si(CH_3)_2$], 0.86 [s, 9H, $SiC(CH_3)_3$], 1.70 (m, XX′ part of AA′XX′ system, $^3J_{AX} + {}^3J_{AX'} = 15.4$, $^3J = 6.1$ Hz, 2H, $CH_2CH_2CH_2O$), 2.48 (dm, AA′ part of AA′XX′ system, $^3J_{AX} + {}^3J_{A'X} = 15.4$, $^4J = 1.4$ Hz, 2H, $CH_2CH_2CH_2O$), 3.63 (t, $^3J = 6.1$ Hz, $CH_2CH_2CH_2O$), 6.56 (dt, $^4J = 2.3$, 1.4 Hz, 1H, 3-H), 6.68 (dd, $^3J = 10.1$, $^4J = 2.3$ Hz, 1H, 5-H), 6.73 (d, $^3J = 10.1$ Hz, 1H, 6-H). – ^{13}C NMR ($CDCl_3$): δ = −5.6 [q, $Si(CH_3)_2$], 18.0 [s, $SiC(CH_3)_3$], 25.6 (t, $CH_2CH_2CH_2O$), 25.7 [q, $SiC(CH_3)_3$], 30.6 (t, $CH_2CH_2CH_2O$), 61.8 (t, $CH_2CH_2CH_2O$), 132.3, 136.0, 136.5 (d, C-3, -5, -6), 149.1 (s, C-2), 187.0, 187.3 (s, C-1, -4). – MS, *m/z* (%): 282 (2) [$M^+ + 2H$], 223 (76), 207 (70). – $C_{15}H_{24}O_3Si$ (280.4): calcd. C 64.25, H 8.63; found C 64.22, H 8.83.

26: IR (film): $\tilde{\nu}$ = 1650 cm^{-1} (C=O). – ^1H NMR ($CDCl_3$): δ = −0.05, −0.03 [s, 6H, $Si(CH_3)_2$], 0.81 [s, 9H, $SiC(CH_3)_3$], 1.12 (d, $^3J = 7.0$ Hz, 3H, CH_3CHCH_2), 3.09 (qddd, $^3J = 7.0$, 5.5, 5.2, $^4J = 1.0$ Hz, 1H, CH_3CHCH_2), 3.51–3.67 (AB system, $\delta_A = 3.63$, $\delta_B =$

3.55, $^2J_{AB}$ = 10.0, ^3J_A = 5.5, ^3J_B = 5.2 Hz, 2H, $CH_3CHCH_AH_B$), 6.56 (dd, ^4J = 2.3, 1.0 Hz, 1H, 3-H), 6.68 (dd, ^3J = 10.1, ^4J = 2.3 Hz, 1H, 5-H), 6.73 (d, ^3J = 10.1 Hz, 1H, 6-H). – ^{13}C NMR ($CDCl_3$): δ = −5.6 [q, $Si(CH_3)_2$], 15.4 (q, CH_3CHCH_2), 18.1 [s, $SiC(CH_3)_3$], 25.9 [q, $SiC(CH_3)_3$], 34.5 (d, CH_3CHCH_2), 66.0 (t, CH_3CHCH_2), 132.5, 135.8, 136.8 (d, C-3, -5, -6), 151.0 (s, C-2), 186.9, 187.6 (s, C-1, -4). – MS, *m/z* (%): 282 (2) [M^+ + 2H], 223 (83), 207 (39). – $C_{15}H_{24}O_3Si$ (280.4): calcd. C 64.25, H 8.63; found C 64.20, H 8.69.

2-(3-Hydroxypropyl)-1,4-benzoquinone (**27a**): A solution of 2.06 g (7.4 mmol) of **25** in 60 ml of acetone and 40 ml of 1 M HCl was stirred for 30 min at room temp. To the solution was then added 50 ml of water, and the mixture was saturated with sodium chloride. Extraction with diethyl ether (5 × 50 ml), drying of the combined extracts ($MgSO_4$), evaporation of the ether and flash chromatography of the residue (diethyl ether/petroleum ether, 2:1) afforded 0.95 g (78%) of **27a**. – IR (Film): $\tilde{\nu}$ = 3350 cm^{-1} (OH), 1650 (C=O). – ^{1}H NMR ($CDCl_3$): δ = 1.75 (m, ^3J = 7.7 Hz, 2H, $CH_2CH_2CH_2O$), 2.51 (dm, ^4J = 1.3 Hz, 2H, $CH_2CH_2CH_2O$), 3.65 (t, ^3J = 7.7 Hz, 2H, $CH_2CH_2CH_2O$), 6.55–6.78 (ABX system, δ_A = 6.56, δ_B = 6.57, δ_X = 6.75, $^3J_{BX}$ + $^5J_{AX}$ = 9.1, $^4J_{AB}$ = 2.9 Hz, 3-, 5-, 6-H). – ^{13}C NMR ($CDCl_3$): δ = 25.4 (t, $CH_2CH_2CH_2O$), 30.46 (t, $CH_2CH_2CH_2O$), 61.3 (t, $CH_2CH_2CH_2O$), 132.5, 136.1, 136.6 (d, C-3, -5, -6), 149.0 (s, C-2), 187.4, 187.7 (s, C-1, -4). – MS, *m/z* (%): 166 (54) [M^+], 150 (18), 148 (60), 138 (100). – $C_9H_{10}O_3$ (166.2): calcd. C 65.05, H 6.07; found C 65.20, H 6.08.

2-[3-(Propionyloxy)propyl]-1,4-benzoquinone (**27b**): 179 mg (1.08 mmol) of **27a** was allowed to react, as described for **14a**, with 120 mg (1.3 mmol) of propionyl chloride and 109 mg (1.38 mmol) of pyridine to afford 176 mg (73%) of **27b**. – IR (Film): $\tilde{\nu}$ = 1730 cm^{-1} (C=O, ester), 1650 (C=O, quinone). – ^{1}H NMR ($CDCl_3$): δ = 1.12 (t, ^3J = 7.5 Hz, 3H, CH_3CH_2), 1.85 (tm, ^3J = 6.3 Hz, 2H, $CH_2CH_2CH_2O$), 2.30 (q, ^3J = 7.5 Hz, 2H, CH_3CH_2), 2.49 (dm, ^4J = 1.4 Hz, 2H, $CH_2CH_2CH_2O$), 4.10 (t, ^3J = 7.5 Hz, 2H, $CH_2CH_2CH_2O$), 6.57 (dt, ^4J = 2.3, 1.4 Hz, 1H, 3-H), 6.70 (dd, ^3J = 10.1, ^4J = 2.3 Hz, 1H, 5-H), 6.75 (d, ^3J = 10.1 Hz, 1H, 6-H). – ^{13}C NMR ($CDCl_3$): δ = 8.9 (q, CH_3CH_2), 25.6, 26.6, 27.3 (t, $CH_2CH_2CH_2O$, CH_3CH_2), 63.0 (t, $CH_2CH_2CH_2O$), 132.5, 136.1, 136.6 (d, C-3, -5, -6), 148.2 (s, C-2), 174.1 (s, $CH_2CH_2CO_2$), 187.0, 187.3 (s, C-1, -4). – MS, *m/z* (%): 224 (3) [M^+ + 2H], 166 (24), 148 (99). – $C_{12}H_{14}O_4$ (222.2): calcd. C 64.85, H 6.35; found C 64.82, H 6.37.

Anodic Oxidation of Hydroquinones

Oxidation of Hydroquinone (**32**): In a divided double-walled beaker-type cell 0.500 g (4.5 mmol) of **32** in 100 ml of a 0.1 M lithium perchlorate solution in anhydrous acetonitrile was electrolyzed at a platinum foil anode (4 cm^2) at 0.9 V vs. Ag/Ag^+ at 15°C until 550 Faraday were consumed. The catholyte consisted of 30 ml of a 0.1 M lithium perchlorate solution in acetonitrile (cathode: 2 cm^2, diapragm: G4 glass frit). For workup the anolyte was neutralized with an aqueous potassium carbonate solution, then concentrated, and the residue was stirred for 2 h with 100 ml of diethyl ether. The supporting electrolyte was filtered off and washed with diethyl ether. The combined ethereal solutions were dried ($MgSO_4$), and the ether was evaporated. Flash chromatography (dichloromethane) of the residue afforded 0.22 g (45%) of benzoquinone (**23**). During evaporation of diethyl ether **23** was partially lost, which accounted for the unfavorable mass balance.

Oxidation of Tetrachlorobenzohydroquinone (**33**): 248 mg (1.00 mmol) of **33** was oxidized, as described for **32**, at 1.2 V vs. Ag/Ag^+ until 189.5 Faraday were consumed. After workup 207 mg (84%) of tetrachlorobenzoquinone (**29**) and 18.1 mg (7.3%) of **33** were obtained.

Oxidation of Hydroquinone **5**: 250 mg (1.0 mmol) of **5** was oxidized, as described for **32**, at 1.1 V vs. Ag/Ag^+ until 185 Faraday were consumed. After workup 152 mg (61.2%) of **4** was obtained.

Oxidation of Hydroquinone **34**: 100 mg (0.33 mmol) of **34** was oxidized, as described for **32**, at 0.8 V vs. Ag/Ag^+ until 50.8 Faraday were consumed. Workup afforded 75.6 mg (76%) of **1c**.

Oxidation of Diethyl 1,4-Dihydro-2,4,6-trimethylpyridine-3,5-dicarboxylate (**35**) *with Quinone* **4**: A solution of 0.67 g (2.5 mmol) of **35** and 0.91 g (3.6 mmol) of **4** in 50 ml of acetonitrile was stirred for 2 h at room temp., and the solvent was subsequently evaporated. Flash chromatography of the residue afforded 0.65 g (88%) of *diethyl 2,4,6-trimethylpyridine-3,5-dicarboxylate* (**36**), n_D^{20} = 1.4952 (ref.[55] 1.4945).

Oxidation of Alkenes with Benzoquinones

Preparation of Ethyl 2-oxo-1-(prop-2-enyl)cyclohexanecarboxylate (**41a**): According to the general procedure for the alkylation of β-dicarbonyl compounds[56] 2.7 g (0.12 mol) of sodium and 16.1 g (95 mmol) of ethyl 2-oxocyclohexanecarboxylate in 150 ml of anhydrous ethanol were stirred for 30 min. Then 10.5 ml (121 mmol) of allyl bromide was slowly added to keep the solution at reflux. After stirring overnight at room temp., the solvent was evaporated, and to the residue was added so much water that the salt just dissolved. The mixture was subsequently extracted with diethyl ether (3 × 100 ml). After drying of the combined ethereal solutions distillation afforded 16.3 g (82%) of **41a**. B.p. 79–82°C/1 Torr, n_D^{20} = 1.4650. – IR (Film): $\tilde{\nu}$ = 1720 cm^{-1} (C=O). – ^{1}H NMR ($CDCl_3$)[57]: δ = 1.20 (t, ^3J = 7.1 Hz, 3H, OCH_2CH_3), 1.32–1.80, 1.90–2.03, 2.35 (m, 8H, $[CH_2]_4$), 2.28, 2.56 (AB system, $^2J_{AB}$ = 13.9, ^3J_A = 7.8, ^3J_B = 7.0 Hz, 2H, $CH_AH_BCH=CH_2$), 4.13 (q, ^3J = 7.1 Hz, 2H, OCH_2CH_3), 4.94–5.05 (m, 2H, $CH_2CH=CH_2$), 5.70 (ddm, ^3J = 7.8, 7.0 Hz, 1H, $CH_2CH=CH_2$). – ^{13}C NMR ($CDCl_3$): δ = 16.0 (q, OCH_2CH_3), 22.2, 27.9, 35.5, 40.6 (t, $[CH_2]_4$), 39.1 (t, $CH_2CH=CH_2$), 60.6 (s, C-1), 61.0 (t, OCH_2CH_3), 118.0 (t,

Table 8. Pd(II)-catalyzed oxidation of 1-octene (**40**) with benzoquinones

Quinone	Solvent	Solvent/ Water	$PdCl_2$ [mmol]	Temp.	Yield (%) **42**
23	DMF	10:1	0.1	room temp.	87
23	DMF	10:1	0.1	60°C	79
23	CH_3CN	10:1	0.1	room temp.	48
23	DMSO	10:1	0.1	room temp.	14
23	Acetone	10:1	0.1	room temp.	77
23	DMF	20:1	0.1	room temp.	81
23	DMF	8:1	0.1	room temp.	91
23	DMF	5:1	0.1	room temp.	88
23	DMF	2:1	0.1	room temp.	84
23	DMF	8:1	0.05	room temp.	91
23	DMF	8:1	0.01	room temp.	77
5	DMF	8:1	0.05	room temp.	11
5	DMF	8:1	0.05	60°C	22
29	DMF	8:1	0.05	room temp.	36
2b	DMF	8:1	0.05	room temp.	13
2c	DMF	8:1	0.05	room temp.	7
1b	DMF	8:1	0.05	room temp.	82
1b	DMF	8:1	0.05	60°C	83
1c[a]	DMF	8:1	0.05	room temp.	51
1c	DMF	8:1	0.05	60°C	74
28	DMF	8:1	0.05	room temp.	11

[a] Reaction time: 24 h.

$CH_2CH{=}CH_2$), 133.1 (d, $CH_2CH{=}CH_2$), 171.2 (s, $CO_2C_2H_5$), 207.2 (s, C-2). – MS, *m/z* (%): 210 (20) [M^+], 182 (12), 165 (22), 137 (100).

Oxidation of Alkenes with Equimolar Amounts of Quinone

Oxidation of 1-Octene (**40**)

a) *Analytical Runs:* 1.1 mmol of quinone and 1 mmol of 1-octene were stirred with palladium dichloride in 2 ml of a solvent/water mixture for 4 h. Subsequently, 20 ml of water was added, and the mixture was extracted with diethyl ether (2 × 25 ml). To the combined ethereal extracts 2-hexanone was added as a GC standard. After filtration of the sample over silica gel (petroleum ether/diethyl ether, 2:1) the yield of 2-octanone (**42**) was determined by GC (glass column). The yields are compiled in Table 8.

b) *Preparative Conversion:* 2.99 g (27.7 mmol) of **23**, 2.83 g (25.2 mmol) of **40**, and 220 mg (1.24 mmol) of palladium dichloride were stirred in 50 ml of DMF/water (8:1) for 5 h at room temp. Subsequently, 150 ml of water was added, excess **23** was reduced with sodium dithionite, and the mixture was then extracted with petroleum ether (5 × 80 ml). The combined extracts were distilled after drying ($MgSO_4$) with a split-tube column to afford 2.66 g (83%) of 2-octanone (**42**). B.p. 170°C, n_D^{20} = 1.4152 (ref.[58] 1.4151).

Oxidation of **41a**: 0.210 g (1 mmol) of **41a**, 1.1 mmol of quinone, and 0.05 mmol of palladium dichloride were stirred in 2 ml of DMF/water (8:1) for 5 h at room temp. For workup 20 ml of a saturated sodium chloride solution was added to the mixture, excess quinone was reduced with sodium dithionite, the mixture was extracted with petroleum ether/diethyl ether (2:1) (4 × 25 ml), the combined extracts were dried ($MgSO_4$), and the solvent was evaporated. CC (petroleum ether/diethyl ether, 2:1) of the residue afforded an unpolar fraction containing **41a** and **44** and a polar fraction containing **43**. The results are compiled in Table 9.

Table 9. Yield of **43** in the palladium(II)-catalyzed oxidation of **41a** with benzoquinones

Experiment No.	Quinone	Yield (%) **43**	Yield[a] (%) **41a + 44**	Mass balance (%)
1	**23**	87	9	96
2	**1b**	77	5	82
3	**1c**	67	7	74
4	**29**	8	69	77
5	**45**	86	5	91
6	**39**	78	11	89
7	**37**	24	63	87

[a] The ratio **44/41a** is larger than 8:1, except in experiments 4 (1:7) and 7 (1:10).

Ethyl 2-Oxo-1-(2-oxopropyl)cyclohexanecarboxylate (**43**): n_D^{20} = 1.4687 (ref.[59] 1.4675). – IR (Film): $\tilde{\nu}$ = 1710 cm^{-1} (C=O). – ^1H NMR ($CDCl_3$): δ = 1.21 (t, ^3J = 7.2 Hz, 3H, CH_2CH_3), 1.55–1.80, 1.90–2.10, 2.25–2.50, 2.65–2.80 (m, 8H, $[CH_2]_4$), 2.70–2.90 [AB system, δ_A = 2.83, δ_B = 2.70, $^2J_{AB}$ = 17.1 Hz, $CH_AH_BC(C{=}O)CH_3$], 4.10–4.25 (AB system, δ_A = 4.19, δ_B = 4.17, $^2J_{AB}$ = 10.7, ^3J = 7.2, 7.2 Hz, 2H, $CH_3CH_AH_B$). – ^{13}C NMR ($CDCl_3$): δ = 13.6 (q, CH_2CH_3), 21.6, 26.5, 36.3, 40.1 (t, $[CH_2]_4$), 29.9 (q, $CH_3C{=}O$), 47.7 (t, CH_2COCH_3), 61.0 (s, C-1), 171.5 (s, $CO_2C_2H_5$), 206.9 (s, $CH_3C{=}O$). – MS, *m/z* (%): 226 (0.7) [M^+], 198 (2), 180 (44), 153 (17). – $C_{12}H_{18}O_4$ (226.3): calcd. C 63.70, H 8.02; found C 63.59, H 8.10.

Ethyl 2-oxo-1-[(E)-prop-1-enyl]cyclohexanecarboxylate (**44**): n_D^{20} = 1.4725. – IR (Film): $\tilde{\nu}$ = 1710 cm^{-1} (C=O). – ^1H NMR ($CDCl_3$): δ = 1.22 (t, ^3J = 7.2 Hz, 3H, OCH_2CH_3), 1.50–1.80, 1.90–2.05, 2.25–2.65 (m, 8H, $[CH_2]_4$), 1.69 (dd, ^3J = 6.7, ^4J = 1.7 Hz, 3H, $CH_3C{=}CH$), 4.05–4.25 (AB system, δ_A = 4.19, δ_B = 4.15, $^2J_{AB}$ = 10.6, ^3J = 7.2, 7.2 Hz, 2H, $CH_3CH_AH_B$), 5.50 (dq, $^3J_{trans}$ = 16.1, ^3J = 6.7 Hz, 1H, $CH{=}CH{-}CH_3$), 5.80 (dq, $^3J_{trans}$ = 16.1, ^3J = 1.7 Hz, 1H, $CH{=}CHCH_3$). – ^{13}C NMR ($CDCl_3$): δ = 13.9 (q, OCH_2CH_3), 18.2 (q, $CH{=}CHCH_3$), 22.4, 27.2, 36.1, 40.6 (t, $[CH_2]_4$), 61.3 (t, OCH_2CH_3), 62.5 (s, C-1), 127.3, 128.5 (d, $CH{=}CHCH_3$), 170.5 (s, $CO_2C_2H_5$), 206.4 (s, C-1). – MS, *m/z* (%): 210 (19) [M^+], 182 (31), 137 (100). – $C_{12}H_{18}O_3$ (210.3): calcd. C 68.54, H 8.63; found C 68.39, H 8.56.

Electrochemical Oxidation of **40**: 21.9 mg (0.20 mmol) of **23** and 4.45 mg (0.025 mmol) of palladium dichloride were dissolved in 8 ml of DMF/water (8:1) that was 0.2 M in lithium perchlorate and was used as the anolyte in a divided microelectrolysis cell. As anode glassy carbon (11 mm^2) and as cathode a platinum foil (1 cm^2) were used. As catholyte 8 ml of 0.2 M lithium perchlorate in DMF/water (8:1) was employed. The diaphragm was a G3 glass frit. At a potential of 1.0 V vs. SCE 119 mg (1.0 g mmol) of **40** was added to the anolyte in small portions within 14 h. After consumption of 180 Faraday, 50 ml of water was added to the anolyte, and the mixture was extracted with diethyl ether (4 × 25 ml). After the addition of 2-hexanone as GC standard and filtration of the combined ethereal solution over silica gel, **42** was obtained in 75% yield as determined by GC.

Electrochemical Oxidation of **41a**: 1.0 mmol of **41a** was oxidized, as described for **40**, in the presence of 0.2 mmol of quinone and 0.05 mmol of palladium dichloride. In this case **41a** was added in one portion at the beginning of the electrolysis. For workup 25 ml of a saturated sodium chloride solution was added to the anolyte, then the mixture was extracted with petroleum ether/diethyl ether (2:1) (4 × 25 ml). The products were separated by column chromatography. The yields for different quinones are listed in Table 10.

Table 10. Yield of **43** in the palladium(II)-catalyzed anodic oxidation of **41a**

Experiment No.	Quinone	Yield (%) **43**	Yield (%) **41a + 44**	Mass balance (%)	Current yield (%)
1	**23**	79	8	87	84
2	**1b**	77	13	90	86
3	**27b**	82	9	91	82

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