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Synthesis of Cinnamaldehydes by Oxidation of Arylpropenes with 2,3-Dichloro-5,6-dicyanoquinone

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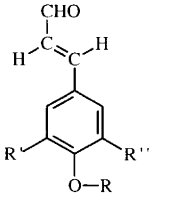
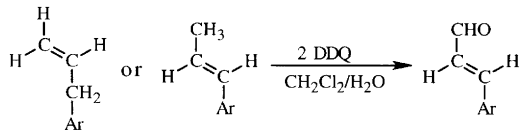
Alkoxylated 1-aryl-1-propenes [1-(4-methoxyphenyl)-1-propene, 1-(3,4-dimethoxyphenyl)-1-propene, 1-(3,4,5-trimethoxyphenyl)-1-propene] and 3-aryl-1-propenes [3-(4-methoxyphenyl)-1-propene, 3-(3,4-dimethoxyphenyl)-1-propene, 3-(3,4,5-trimethoxyphenyl)-1-propene] gave cinnamaldehydes in 71–84% yield on treatment with 2,3-dichloro-5,6-dicyanoquinone (DDQ) (slight excess) at room temperature for 0.5 2 h in the two-phase system dichloromethane–water (4:1). Arylpropenes lacking electron-donating alkoxy groups (1-phenyl-1-propene, 3-phenyl-1-propene) or carrying an acetoxy group [1-(4-acetoxy-3-methoxyphenyl)-1-propene, 3-(4-acetoxy-3-methoxyphenyl)-1-propene] were converted into cinnamaldehydes in low to moderate yields on oxidation with a large excess of DDQ in combination with long reaction times (>12 h). All the 1-aryl-1-propenes examined were rapidly converted into a mixture of mono- and bis-(3-aryl-2-propenyl) ethers of 2,3-dichloro-5,6-dicyanohydroquinone (DDHQ) on DDQ oxidation. The rate of formation of DDHQ ethers from alkoxy-substituted 3-aryl-1-propenes was slightly lower. 3-Phenyl-1-propene and also 3-(4-acetoxy-3-methoxyphenyl)-1-propene were largely unchanged at the initial stage of the oxidation. Significant differences in the compositions of the DDHQ ether mixtures obtained from 1-aryl-1-propenes and 3-aryl-1-propenes were not observed.

A few percent of the phenylpropane units in lignins are end groups of type **1**, and cinnamaldehydes of type **1** are known to form on acidolytic degradation of lignins.[1] Cinnamaldehydes of type **1** are also frequently found in plant extractives (see, e.g., Ref. 2). Quite a few methods for the synthesis of aldehydes of this type have been published.[3] One such method is based on the oxidation of arylpropenes with 2,3-dichloro-5,6-dicyanoquinone (DDQ) in the presence of water[4–9] (regarding the use of DDQ as oxidant in organic chemistry, see Ref. 10). This paper describes an examination of the scope of this synthetic method and its use for the synthesis of a series of cinnamaldehydes (for a preliminary report, see Ref. 11). The arylpropenes were oxidized with DDQ at room temperature using the two-phase system dichloromethane–water (4:1) as reaction medium (Scheme 1). Previous studies[6,12] suggest that the formation of cinnamaldehydes proceeds via ethers of 2,3-dichloro-5,6-dicyanohydroquinone (DDHQ) of types **2** and **3**. A ^{1}H NMR spectrometric method for the analysis of such intermediates in the oxidation products was worked out. Application of this analytical method made it possible to judge the completeness of the conversion

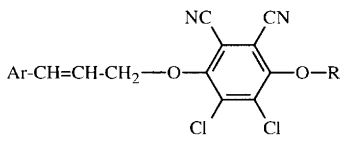


R = C or H, R' and R''= H, O or C

1



Scheme 1.



2 R= H
3 R= Ar-CH=CH-CH$_2$

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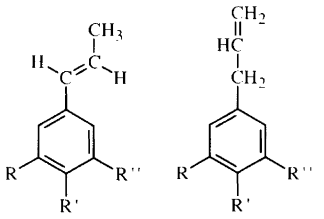


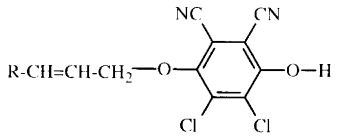
4a **4b** R=R''= H, R'= OCH_3
5a **5b** R= H, R'=R''= OCH_3
6a **6b** R=R'=R''= OCH_3
7a **7b** R=R'=R''= H
8a **8b** R=H, R'= $OCOCH_3$, R''= OCH_3

of the arylpropenes into aldehydes. Oxidation experiments with a variety of arylpropenes [(*E*)-1-aryl-1-propenes **4a**–**8a** and 3-aryl-1-propenes **4b**–**8b**] showed that cinnamaldehydes could be obtained in good yields provided the aromatic ring carried electron-donating alkoxy-substituents. Cinnamaldehydes of type **1** can be prepared by DDQ oxidation of alkoxy-substituted starting materials or alkoxy-substituted synthetic intermediates. DDQ oxidation of arylpropenes is therefore a feasible method for the preparation of such cinnamaldehydes.

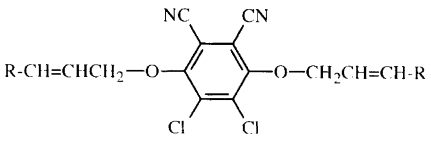
Analysis of intermediate DDHQ ethers

Kiefer and Lutz[6] obtained evidence for the intermediacy of DDHQ ethers in the DDQ oxidation of 1-aryl-1-propenes and 3-aryl-1-propenes leading to cinnamaldehydes. They have described the DDHQ monoethers **9a** and **10a** and also the diethers **9b** and **10b**. We have subjected these compounds to complementary spectral examinations (see the Experimental). Although the ^1H NMR spectra of the monoethers and the diethers are very similar, it was possible to analyse them in the crude DDQ oxidation products of **4** and **7**: signals from the methylene groups appeared at $\delta \approx 5$ and the signal from the diether (**9b** or **10b**) was located at somewhat lower field (≈ 0.05 δ units) than the signal from the corresponding monoether (**9a** or **10a**) (Table 1). We assume that this also holds true for the analogous DDHQ ethers detected (see below) in the oxidation products obtained from **5**, **6** and **8** (Table 1). Acetone was used as the solvent in the ^1H NMR studies since the solubility of the oxidation products in chloroform is limited.

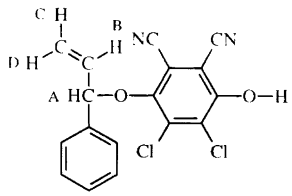
Examination of the reaction mixtures obtained on treatment of **4**–**6** with 1.2 mol DDQ/mol substrate showed that they were converted into DDHQ ethers within a short period of time. The 1-aryl-1-propenes (**4a**–**6a**) reacted somewhat more rapidly than the 3-aryl-1-propenes (**4b**–**6b**). Similar experiments with **7** and **8** showed that the 1-aryl-1-propenes (**7a** and **8a**) were rapidly converted into DDHQ ethers while the 3-aryl-1-propenes (**7b** and **8b**) were largely unchanged at the initial stage of the oxidation. In a second series of experiments **7** and **8** were oxidized with DDQ (mol DDQ/mol arylpropene ratio 2.4 : 1) for 3 h. DDHQ ethers were the main constituents in the reaction mixtures



9a R= phenyl
10a R= 4-methoxyphenyl
11a R= 3,4-dimethoxyphenyl
12a R= 3,4,5-trimethoxyphenyl
13a R= 4-acetoxy-3-methoxyphenyl



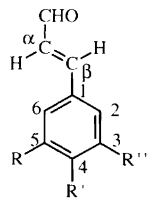
9b R= phenyl
10b R= 4-methoxyphenyl
11b R= 3,4-dimethoxyphenyl
12b R= 3,4,5-trimethoxyphenyl
13b R= 4-acetoxy-3-methoxyphenyl



9c

Table 1. ^1H NMR signals from methylene groups in DDHQ ethers of types **2** and **3** (solvent, deuterioacetone).

Compound	δ value (J/Hz)
9b	4.99 (1.2, 6.8)
9a	4.94 (1.2, 6.8)
10b	4.96 (1.2, 6.8)
10a	4.91 (1.0, 6.9)
11b	4.95 (6.8)
11a	4.90 (6.8)
12b	4.96 (0.8, 6.8)
12a	4.90 (0.8, 6.8)
13b	4.98 (1.2, 6.8)
13a	4.93 (1.0, 6.8)



14 R=R'=R''= H
15 R=R''=H, R'=OCH_3
16 R=H, R'=R''=OCH_3
17 R=R'=R''=OCH_3
18 R=H, R'=$OCOCH_3$, R''=OCH_3

obtained from the 1-aryl-1-propenes (**7a** and **8a**); as expected no starting material remained. The starting materials were the main constituents in the reaction mixtures obtained from the 3-aryl-1-propenes (**7b** and **8b**) but substantial amounts of DDHQ were also present. The yields of cinnamaldehydes (**14**, **18**) were 3–4% from the 3-aryl-1-propenes (**7b** and **8b**) and 4–5% from the 1-aryl-1-propenes (**7a** and **8a**). The comparatively low reactivity of **7b** and DDHQ ethers **9a** and **9b** on DDQ oxidation is probably a consequence of the absence of electron-donating substituents on the aromatic ring. The presence of the comparatively weakly electron-donating acetoxy-substituent and the substitution pattern at the aromatic ring in **8b**, **13a** and **13b** may explain the low reactivity of these compounds.

Significant differences in the compositions of the DDHQ ether mixtures obtained from 1-aryl-1-propenes and 3-aryl-1-propenes were not observed. The amounts of monoethers were larger than the amounts of diethers in all the reaction mixtures examined.

^{1}H NMR spectral examinations of oxidation products obtained from **7a**/**7b** revealed the presence of small amounts of a compound that was tentatively identified as **9c**. Re-examination of the oxidation products of **8a** indicated that small amounts of the analog of **9c** are formed on DDQ oxidation of this substrate.

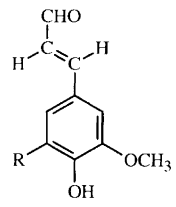
Synthesis of cinnamaldehydes

Arylpropenes **4**–**6** gave the corresponding cinnamaldehydes **15**–**17** in 71–84% yield on oxidation with DDQ (mol DDQ/mol substrate ratio 2.2 or 2.5) for 0.5–2 h at room temperature using the two-phase system dichloromethane–water (4 : 1) as reaction medium. The reaction product obtained from **6b** contained a few percent DDHQ ethers even after a reaction time of 2 h (no starting material was present). No DDHQ ethers or starting materials could be detected in the reaction mixtures obtained from the other substrates. In contrast with what would be expected from earlier work,[6] the yields of cinnamaldehydes obtained from the 3-aryl-1-propenes (**4b**–**6b**) were about as high as the yields obtained from the 1-aryl-1-propenes (**4a**–**6a**).

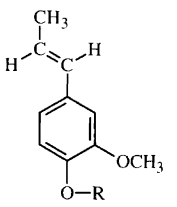
Excess DDQ in the oxidation mixtures was reduced to DDHQ by treatment with ascorbic acid. Solids were filtered off and the aqueous and organic layers were separated. Minor amounts of polymeric materials are formed on DDQ oxidation of arylpropenes (cf. Ref. 6). It was found that the polymers, at least in some instances, were present as a colloid in the organic layer. Extraction with brine caused precipitation of the polymers. Drying and removal of the solvent gave the crude oxidation product. The described work-up procedure does not remove DDHQ ethers and is therefore the preferred one when it is of interest to record the occurrence of such compounds in the oxidation products. Replacement of the extraction with brine by extraction with saturated sodium bicarbonate solution gave crude products consisting of almost pure cinnamaldehydes (^{1}H NMR). Remaining contaminants (some of them are strongly colored) were removed by column chromatography and recrystallizations. Extraction with sodium bicarbonate solution removed dissolved DDHQ and DDHQ monoethers. DDHQ is a strongly acidic phenol ($pK_a1 = 5.14$ and $pK_a2 = 7.46$ in dimethylformamide–H_2O 7 : 3[13]).

It was found that the 1-aryl-1-propene **8a** could be converted into **18** in 40% yield by DDQ oxidation for 12 h using a large excess of DDQ (mol DDQ/mol arylpropene ratio 5 : 1). Large amounts of DDHQ ethers **13a** and **13b** were present in the crude product. Gierer *et al.*[9] have reported the formation of **18** in 35% yield on oxidation of **8b** with DDQ for 72 h. Coniferaldehyde (**19**) can be obtained from **18** by hydrolysis of the acetate group. It is evident that the preparation of **19** from **21** or **23** via DDQ oxidation of their acetates gives rather low yields. Nakamura and Higuchi[8] obtained coniferaldehyde in good yield by DDQ oxidation of the methoxymethyl derivative of **21** (i.e., compound **22**) and subsequent deprotection. Preliminary experiments showed that DDQ oxidation can be favorably applied to the synthesis of coniferaldehyde (**19**) and sinapylaldehyde (**20**) from **23** and **24**, respectively.[14] DDQ oxidation of the methoxymethyl derivative of **23** and **24** as well as the tetrahydropyran-2-yl derivatives of **23** gave, after deprotection, **19**/**20** in yields similar to those obtained for **15**–**17** in the oxidation experiments with **4**–**6**.

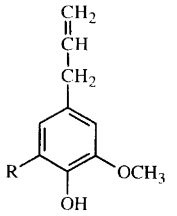
It was mentioned in the introductory section of this paper that cinnamaldehydes such as **19** and **20** are well known as constituents in plant extractives and as lignin degradation products. End groups in lignin of the cinnamaldehyde type (**1**) are in general attached to the lignin by ether linkages. The synthesized cinnamaldehydes **15**–**17** are appropriate model compounds for such end groups.



19 R= H
20 R= OCH_3



21 R=H
22 R=CH_2OCH_3



23 R= H
24 R= OCH_3

Experimental

2,3-Dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) was purchased from Aldrich. Dichloromethane washed with and saturated with water (water content: 0.198% by weight at 25 °C[15]) was used as reaction medium in all the oxidation experiments with DDQ. Merck Silica gel 60 (230–400 mesh) and Merck Aluminium oxide active neutral (70–230 mesh) were used for column chromatography.

NMR Spectra. ^{1}H NMR spectra were recorded at 400 MHz and ^{13}C NMR spectra at 100.6 MHz with a Varian XL-400 (VXR-5000) instrument; $T \approx 20$ °C. Deuteriochloroform was used as the solvent unless otherwise specified [internal reference, $(CH_3)_4Si$].

Mass spectrometry (MS). MS was carried out with a ZabSpec magnetic sector instrument (VG Analytical, Fisons instrument); polyfluorinated kerosene (PFK) was used as the reference compound.

Thin layer chromatography (TLC) was performed on silica gel plates (Merck, Kieselgel 60 F_{254}) with toluene–ethyl acetate (10:1) as the eluent. R_f values: **15**, 0.32; **16**, 0.14; **17**, 0.14; **18**, 0.16. Spots were made visible with UV light and by treatment with *p*-anisaldehyde–ethanol–H_2SO_4–acetic acid (5:186:7:2) and subsequent heating.

Standard procedure for column chromatography. Crude DDQ oxidation products were purified by chromatography on a column (40 g SiO_2 with 15 g Al_2O_3 at the top) using toluene–ethyl acetate (10:1) as the eluent. The fractions containing the materials of interest were pooled on the basis of TLC examinations.

3-(3,4,5-Trimethoxyphenyl)-1-propene (**6b**). 4-Allyl-2,6-dimethoxyphenol (**24**) (Aldrich, technical grade) was methylated by a method applied to the preparation of the methyl ester of (2,6-dimethoxyphenoxy)ethanoic acid.[16] The product was purified by column chromatography [SiO_2; eluent, dichloromethane–ethyl acetate (20:1)]. ^{1}H NMR spectrum; δ 3.34 (2 H, br d, J = 6.8 Hz, Ar–CH_2), 3.83 (3 H, s, OCH_3), 3.85 (6 H, s, OCH_3), 5.05–5.15 (2 H, m, =CH_2), 5.96 (1 H, ddt, J = 16.8, 10.0 and 6.8 Hz, vinyl –CH=), 6.41 (2 H, s, H–Ar).

(E)-1-(3,4,5-Trimethoxyphenyl)-1-propene (**6a**) was prepared by methylation (cf. the preparation of **6b**) of 2,6-dimethoxy-[(*E*)-1-propenyl]phenol.[17] ^{1}H NMR spectrum of **6a**: δ 1.88 (3 H, dd, J = 1.4 and 6.7 Hz, CH_3–C), 3.83 (3 H, s, OCH_3), 3.87 (6 H, s, OCH_3), 6.15 (1 H, dq, J = 15.8 and 6.7 Hz, vinyl H), 6.33 (1 H, dd, J = 1.4 and 15.8 Hz, vinyl H), 6.55 (2 H, s, H–Ar).

(E)-3-(3,4-Dimethoxyphenyl)propenal (**16**). *Method A.* The procedure described in Ref. 11 was followed. Starting material: 3-(3,4-dimethoxyphenyl)-1-propene (**5b**).

Method B. Water (40 ml) and DDQ (8.8 mmol) were added to a solution of 3-(3,4-dimethoxyphenyl)-1-propene (**5b**) (4 mmol) in water-saturated dichloromethane (160 ml). The mixture was magnetically stirred for 1 h at room temperature. A solution of ascorbic acid (8.8 mmol) in 40 ml water was added to the reaction mixture and stirring was continued for 10 min. Solids were filtered off and the liquid layers were separated. The organic layer was washed with a saturated solution of $NaHCO_3$ (100+50 ml) and water (50 ml). Drying (Na_2SO_4) and evaporation of the solvent gave a crystalline residue (0.73 g, m.p. 75–78 °C) consisting of **16** (^{1}H NMR). Colored contaminants were removed by chromatography on a short aluminium oxide column (10 g Al_2O_3; eluent, dichloromethane). A product (0.69 g) of m.p. 79–80 °C was obtained. Recrystallization from benzene gave a product (0.614 g) of m.p. 83–84 °C (lit.[3h] 83–84 °C). Yield: 80%. ^{13}C NMR spectrum: δ 56.1 (OCH_3), 56.2 (OCH_3), 109–153 (109.9, 111.2, 123.6, 126.8, 127.2, 149.5, 152.1, 153.0) (aromatic and vinyl C), 193.7 (CO).

Method C. Starting material: (*E*)-1-(3,4-dimethoxyphenyl)-1-propene (**5a**) (4 mmol). The procedure for the preparation of **16** by DDQ oxidation of **5b** described in Ref. 11 was followed. Purification by column chromatography (standard procedure) gave a product weighing 0.59 g (m.p. 81 °C). Yield: 77%.

(E)-3-(4-Methoxyphenyl)propenal (**15**). *Method A.* Water (40 ml) and DDQ (10 mmol) were added to a solution of 3-(4-methoxyphenyl)-1-propene (**4b**) (4 mmol) in water-saturated dichloromethane (160 ml). The mixture was magnetically stirred for 2 h at room temperature. A solution of ascorbic acid (10 mmol) in 40 ml water was added to the reaction mixture and stirring was continued for 5 min. Solids were filtered off and the liquid layers were separated. The organic layer was washed with brine (2 × 10 ml) and dried (Na_2SO_4). Column chromatography (standard procedure) of the residue (0.74 g) gave a product (0.55 g) consisting of essentially pure **15** (^{1}H NMR). M.p. 57 °C. Yield: 84%. Recrystallization from benzene–hexane gave a product of m.p. 58 °C (lit.[6] 58–59 °C). ^{1}H NMR spectrum: δ 3.85 (3 H, s, OCH_3), 6.60 (1 H, dd, J = 7.8 and 16 Hz, vinyl H), 6.94 (2 H, m, H–Ar), 7.42 (1 H, d, J = 16 Hz, vinyl H), 7.52 (2H, m, H–Ar), 9.65 (1 H, d, J = 7.8 Hz, CHO). ^{13}C NMR spectrum: δ 55.7 (OCH_3), 114–163 [114.8 (2 C), 126.6, 126.9, 130.6 (2 C), 153.1, 162.4] (aromatic and vinyl C), 194.0 (CO).

Method B. Oxidation of (*E*)-1-(4-methoxyphenyl)-1-propene (**4a**) in an experiment similar to that carried out with **4b** (see above) gave, after purification of the crude product by column chromatography, 0.55 g **15** of m.p. 57 °C (yield, 84%).

(E)-3-(3,4,5-Trimethoxyphenyl)propenal (**17**). *Method A.* 3-(3,4,5-Trimethoxyphenyl)-1-propene (**6b**) (4 mmol) was oxidized with DDQ following the procedure used for the preparation of **15** from **4b** (see above). The crude product (1.2 g) contained a few percent DDHQ ethers (**12a** and **12b**) (^{1}H NMR). Purification by column chromatography (standard procedure) gave a product (0.63 g) consisting of essentially pure **17** (^{1}H NMR). M.p. 112–113 °C (lit.[18] 111 °C). Yield: 71%. Recrystallization from benzene gave 0.50 g product of the same m.p. Some colored contaminants were removed by the recrystallization. ^{1}H NMR spectrum: δ 3.91 (9 H, s, OCH_3), 6.65 (1 H, dd, J = 8 and 16 Hz, vinyl H), 6.80 (2 H, s, H–Ar), 7.41 (1 H, d, J = 16 Hz, vinyl H), 9.69 (1 H, d, J = 8 Hz, CHO). ^{13}C NMR spectrum: 56.4 (2 C, OCH_3), 61.2 (OCH_3), 105.8 (2 C, C-2 and C-6),

128.1 (Cα), 129.6 (C-1), 141.1 (C-4), 152.9 (Cβ), 153.7 (2 C, C-3 and C-5), 193.6 (CO). The assignments are based on HETCOR experiments.

Method B. Oxidation of (*E*)-1-(3,4,5-trimethoxyphenyl)-1-propene (**6a**) in experiments similar to that carried out with **6b** (see above) gave, after purification of the crude product by column chromatography, **17** in 70–80% yield.

(E)-3-(4-Acetoxy-3-methoxyphenyl)propenal (**18**). Water (40 ml) and DDQ (20 mmol) were added to a solution of (*E*)-1-(4-acetoxy-3-methoxyphenyl)-1-propene[19] (**8a**) (4 mmol) in water-saturated dichloromethane (160 ml). The mixture was magnetically stirred for 12 h at room temperature. A solution of ascorbic acid (20 mmol) in 50 ml water was added to the reaction mixture and stirring was continued for 10 min. Solids were filtered off and the liquid layers were separated. The organic layer was washed with brine (3 × 70 ml) and dried (Na_2SO_4). The residue (1.38 g) obtained on evaporation of the solvents consisted primarily of **18** and DDHQ ethers **13a** and **13b** (^{1}H NMR). Column chromatography (standard procedure) gave a product (0.36 g) consisting of essentially pure **18** (^{1}H NMR). M.p. 97–98 °C. Recrystallization from methanol–H_2O raised the m.p. to 98–99 °C (lit.[3g] 98–100 °C). ^{1}H NMR spectrum: δ 2.34 (3 H, s, CH_3CO), 3.89 (3 H, s, OCH_3), 6.68 (1 H, dd, J=8.0 and 15.8 Hz, vinyl H), 7.11 (1 H, d, J=6.5 Hz, H–Ar), 7.15 (1 H, d, J=1.6 Hz, H–Ar), 7.18 (1 H, dd, J=1.6 and 6.5 Hz, H–Ar), 7.45 (1 H, d, J=15.8 Hz, vinyl H), 9.71 (1 H, d, J=8.0 Hz, CHO). ^{13}C NMR spectrum: 20.9 (CH_3–C), 56.2 (OCH_3), 111–153 (111.6, 122.1, 123.7, 128.9, 133.1, 142.4, 151.79, 152.1) (aromatic and vinyl C), 168.9 (CO), 193.7 (CHO).

DDHQ ethers **9a**, **9b** *and* **9c**. Quinol ethers **9a** and **9b** have been described by Kiefer and Lutz.[6] In the present work these DDHQ ethers were isolated from the reaction product obtained on oxidation of (*E*)-1-phenyl-1-propene (**7a**) (6 mmol) with DDQ according the procedure described by Keifer and Lutz[6] for the conversion of (*E*)-1-(4-methoxyphenyl)-1-propene (**4a**) into **15**. Column chromatography (40 g, SiO_2; eluent chloroform) of the crude product gave fractions of **14** (<10 mg), **9b** (140 mg) and **9a** (433 mg). ^{1}H NMR spectrum of **9a** (solvent, deuterioacetone): δ 4.94 (2 H, dd, J=1.0 and 6.8, CH_2), 6.60 (1 H, dt, J=16 and 6.8 Hz, vinyl H), 6.83 (1 H, J=16 Hz, vinyl H), 7.2–7.6 (5 H, m, H–Ar). MS (FAB, matrix glycerol) of **9a** showed a peak at m/z 345.01 (rel. intensity 2.3%) attributed to $(M+H)^+$ (calc. for $C_{17}H_{10}Cl_2N_2O_2$: m/z 345.02). The fragment ion m/z 117.072 was the base peak and it is attributed to the cinnamyl cation (calc. for C_9H_9: m/z 117.070). ^{1}H NMR spectrum of **9b** (solvent, deuterioacetone): δ 4.99 (4 H, dd, J=1.2 and 6.8 Hz, CH_2), 6.59 (2 H, dt, J=16 and 6.8 Hz, vinyl H), 6.83 (2 H, J=16 Hz, vinyl H), 7.2–7.6 (10 H, m, H–Ar). MS (EI, 70 eV; ion source temperature, 220 °C) of **9b**. Molecular ion: m/z 460.076 (rel. intensity 1.4%) (calc. for $C_{26}H_{18}Cl_2N_2O_2$: m/z 460.075). Selected fragment ions: m/z 343.004 (rel. intensity 3.62%; calc. for $C_{17}H_9Cl_2N_2O_2$: m/z 343.004), m/z 227.947 (rel. intensity 45%; calc. for $C_8H_2Cl_2N_2O_2$: m/z 227.949), m/z 117.065 (base peak; calc. for C_9H_9: m/z 117.070).

Examination of the crude product obtained on oxidation (the above described procedure for the preparation of **15** from **4b** was applied, reaction time 30 min) of (*E*)-1-phenyl-1-propene (**7a**) by ^{1}H NMR spectroscopy showed that it consisted primarily of **9a** and **9b** (no starting material was present). The spectrum also revealed the presence of small amounts of an additional compound tentatively identified as the DDHQ ether of 1-phenyl-2-propen-1-ol (**9c**). ^{1}H NMR spectrum: δ 5.35 (1 H, ddd, J=0.8, 1.4 and 10 Hz; H_C), 5.41 (1 H, ddd, J=0.8, 1.4 and 17 Hz, H_D), 5.91 (1 H, d, J=8.4 Hz, H_A), 6.27 (1 H, ddd, J=8.4, 10 and 17 Hz, H_B), 7.1–7.7 (aromatic protons, separate signals from aromatic protons in **9c** could not be discerned).

DDHQ ethers **10a** *and* **10b**. Quinol ethers **10a** and **10b** have been described by Kiefer and Lutz.[6] The crude reaction products obtained on oxidation of a (*E*)-1-(4-methoxyphenyl)-1-propene (**4a**) (cf., the aforementioned experiment with this compound) with 1.2 mol DDQ/mol substrate consisted primarily of **10a**, **10b** and minor amounts of aldehyde **15** (^{1}H NMR). In a separate experiment compound **10a** was removed by replacing brine with saturated $NaHCO_3$ solution in the washing step. ^{1}H NMR spectral data for **10a** and **10b** were derived from examinations of the two reaction products. ^{1}H NMR spectrum of **10a** (solvent, deuterioacetone): 3.81 (3 H, s, OCH_3), 4.91 (2 H, dd, J=1.0 and 6.9 Hz, CH_2), 6.44 (1 H, dt, J=15.8 and 6.9, vinyl H), 6.74 (1 H, d, J=15.8 Hz, vinyl H), 6.90–6.95 (2 H, m, H–Ar), 7.4–7.5 (2 H, m, H–Ar). ^{1}H NMR spectrum of **10b** (solvent, deuterioacetone): 3.81 (6 H, s, OCH_3), 4.96 (4 H, dd, J=1.2 and 6.8 Hz, CH_2), 6.43 (2 H, dt, J=15.8 and 6.8 Hz, vinyl H), 6.74 (2 H, d, J=15.8 Hz, vinyl H), 6.90–6.95 (4 H, m, H–Ar), 7.4–7.5 (4 H, m, H–Ar). (^{1}H NMR spectral data for **10a** and **10b** in chloroform solution are reported elsewhere.[11])

Comparative oxidation experiments with (E)-1-phenyl-1-propene, 3-phenyl-1-propene, (E)-1-(4-acetoxy-3-methoxyphenyl)-1-propene and 3-(4-acetoxy-3-methoxyphenyl)-1-propene. Water (40 ml) and DDQ (9.6 mmol) were added to a solution of the arylpropene (**7a**, **7b**, **8a** or **8b**) (4 mmol) in water-saturated dichloromethane (160 ml). The mixture was magnetically stirred for 3 h at room temperature. A solution of ascorbic acid (9.6 mmol) in 40 ml water was added to the reaction mixture and stirring was continued for 5 min. Solids were filtered off and the liquid layers were separated. The organic layer was washed with brine (2 × 100 ml) and dried (Na_2SO_4). The residue obtained on evaporation of the solvents (note: **7b** is volatile) was examined by ^{1}H NMR spectroscopy (solvent, deuterioacetone). Quantitative estimates

of the constituents in the reaction mixture were made using hexamethylbenzene as an internal standard (signal at δ 2.23), cf. Ref. 20.

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