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

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Alkyolated 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). Arylpropanes lacking electron-donating alkoxy groups [1-phenyl-1-propene, 3-phenyl-1-propene] or carrying an acetox 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-dicyanoquinodimethane (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 arylpropanes with 2,3-dichloro-5,6-dicyanoquinone (DDQ) in the presence of water4–9 (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 arylpropanes were oxidized with DDQ at room temperature using the two-phase system dichloromethane–water (4:1) as reaction medium (Scheme 1). Previous studies6,12 suggest that the formation of cinnamaldehydes proceeds via ethers of 2,3-dichloro-5,6-dicyanoquinodimethane (DDHQ) of types 2 and 3. A 1H 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

![Scheme 1](image)

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of the arylpropanes into aldehydes. Oxidation experiments with a variety of arylpropanes [(E)-1-aryl-1-propanes 4a-8a and 3-aryl-1-propanes 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 arylpropanes 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-propanes and 3-aryl-1-propanes 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 \(^1\)H 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 (\(\approx 0.05 \delta\) 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 \(^1\)H 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-propanes (4a-6a) reacted somewhat more rapidly than the 3-aryl-1-propanes (4b-6b). Similar experiments with 7 and 8 showed that the 1-aryl-1-propanes (7a and 8a) were rapidly converted into DDHQ ethers while the 3-aryl-1-propanes (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 arylpropane ratio 2:4:1) for 3 h. DDHQ ethers were the main constituents in the reaction mixtures.

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\delta) value (L/Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9b</td>
<td>4.99 (1.2, 6.8)</td>
</tr>
<tr>
<td>9a</td>
<td>4.94 (1.2, 6.8)</td>
</tr>
<tr>
<td>10b</td>
<td>4.96 (1.2, 6.8)</td>
</tr>
<tr>
<td>10a</td>
<td>4.91 (1.0, 6.8)</td>
</tr>
<tr>
<td>11b</td>
<td>4.95 (6.8)</td>
</tr>
<tr>
<td>11a</td>
<td>4.90 (6.8)</td>
</tr>
<tr>
<td>12b</td>
<td>4.96 (0.8, 6.8)</td>
</tr>
<tr>
<td>12a</td>
<td>4.90 (0.8, 6.8)</td>
</tr>
<tr>
<td>13b</td>
<td>4.96 (1.2, 6.8)</td>
</tr>
<tr>
<td>13a</td>
<td>4.93 (1.0, 6.8)</td>
</tr>
<tr>
<td>14</td>
<td>R=R' = R'' = H</td>
</tr>
<tr>
<td>15</td>
<td>R=R' = R'' = H, R=OCH(_3)</td>
</tr>
<tr>
<td>16</td>
<td>R=H, R=OCH(_3)</td>
</tr>
<tr>
<td>17</td>
<td>R=R' = R'' = OCH(_3)</td>
</tr>
<tr>
<td>18</td>
<td>R=H, R=OCH(_3), R'=OCH(_3)</td>
</tr>
</tbody>
</table>
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.

31H 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

Arylpropanes 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,9 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 arylpropanes (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 (4H 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 (pKa1 = 5.14 and pKa2 = 7.46 in dimethylformamide-H2O 7:312).

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/mole 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 Higuchi9 obtained coniferaldehyde in good yield by DDQ oxidation of the methoxy-methyl 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.44 DDQ oxidation of the methoxymethyl derivative of 23 and 24 as well as the tetrahydro- pyran-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.

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°C15) 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; $T \approx 20^\circ$ C. Deuteriochloroform was used as the solvent unless otherwise specified [internal reference, (CH$_3$)$_3$Si].

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 were 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$_2$SO$_4$–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$_2$O$_3$ 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, dd, 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-propenylphenol. $^{17}$ $^1$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)propen (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$_2$SO$_4$) 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$_2$O$_3$; 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.$^{3b}$ 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 x 10 ml) and dried (Na$_2$SO$_4$). 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.$^9$ 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 (2 H, 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 0.5 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),
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128.1 (C9), 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-propene19 (8a) (4 mmol) in water-saturated dichloromethane (160 ml). The mixture was magnetically stirred for 12 h at room temperature. A solution of acetic 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 (Na2SO4). The residue (1.38 g) obtained on evaporation of the solvents consisted primarily of 18 and DDHQ ethers 13a and 13b (1H NMR). Column chromatography (standard procedure) gave a product (0.36 g) consisting of essentially pure 18 (1H NMR). M.p. 97–98°C. Recrystallization from methanol–H2O raised the m.p. to 98–99°C (lit.39 98–100°C).1H NMR spectrum: δ 2.34 (3 H, s, CH3CO), 3.89 (3 H, s, OCH3), 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).13C NMR spectrum: 20.9 (CH3-C), 56.2 (OCH3), 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 Kiefer and Lutz6 for the conversion of (E)-1-(4-methoxyphenyl)-1-propene (4a) into 15. Column chromatography (40 g, SiO2; eluent chloroform) of the crude product gave fractions of 14 (<10 mg), 9b (140 mg) and 9a (433 mg).1H NMR spectrum of 9b (solvent, deuteroacetone): δ 4.94 (2 H, dd, J = 1.0 and 6.8, CH2), 6.60 (1 H, dt, J = 16 and 6.8 Hz, vinyl H), 6.83 (1 H, J = 16 Hz, vinyl H), 1.7–7.6 (S 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 C9H6O3Cl2N2O2: 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 C7H5N2: m/z 117.070).1H NMR spectrum of 9b (solvent, deuteroacetone): δ 4.99 (4 H, dd, J = 1.2 and 6.8 Hz, CH2), 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 C26H18O11N2O4: m/z 460.075). Selected fragment ions: m/z 343.004 (rel. intensity 3.62%; calc. for C17H12ClN2O3: m/z 343.004), m/z 227.947 (rel. intensity 45%; calc. for C8H5Cl2N2O2: m/z 227.949), m/z 117.065 (base peak; calc. for C6H6N2: m/z 117.070). Examinations 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 1H 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).1H NMR spectrum: δ 5.35 (1 H, ddd, J = 0.8, 1.4 and 10 Hz, Hc), 5.41 (1 H, ddd, J = 0.8, 1.4 and 17 Hz, Hb), 5.91 (1 H, d, J = 8.4 Hz, Hb), 6.27 (1 H, ddd, J = 8.4, 10 and 17 Hz, Hb), 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 (1H NMR). In a separate experiment compound 10a was removed by replacing brine with saturated NaHCO3 solution in the washing step.1H NMR spectral data for 10a and 10b were derived from examinations of the two reaction products.1H NMR spectrum of 10a (solvent, deuteroacetone): 3.81 (3 H, s, OCH3), 4.91 (2 H, dd, J = 1.0 and 6.9 Hz, CH2), 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).1H NMR spectrum of 10b (solvent, deuteroacetone): 3.81 (6 H, s, OCH3), 4.96 (4 H, dd, J = 1.2 and 6.8 Hz, CH2), 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).1H 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 acetic 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 (Na2SO4). The residue obtained on evaporation of the solvents (note: 7b is volatile) was examined by 1H NMR spectroscopy (solvent, deuteroacetone). Quantitative estimates

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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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References


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