The Reactions of Lignin during Neutral Sulphite Pulping

Part III.* The Mechanism of Formation of Styrene-β-sulphonic Acid Structures

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The mechanism of formation of styrene-β-sulphonic acid structures from phenolic β-arylether structures in lignin during neutral sulphite pulping has been studied. Experimental support is provided for the course of reaction proceeding *via* methylene quinone-, α-sulphonic acid-, and α,β-disulphonic acid structures, as outlined in Scheme 1.

In Part I[2] of this series it has been shown that β-arylether linkages in phenolic phenylpropane units of lignin (I) are extensively cleaved by neutral sulphite yielding the corresponding styrene-β-sulphonic acid structures (III), whereas β-arylether linkages in non-phenolic units (II) remain essentially unaffected. The present work deals with the mechanism of formation of styrene-β-sulphonic acid structures in lignin during neutral sulphite pulping.

The reactivity of the β-aryl ether linkages (I) in phenolic phenylpropane units and the stability of the same type of linkage in non-phenolic phenylpropane units (II) suggest that the phenolic hydroxyl group in the *para*-position relative to the side chains plays an essential part in the cleavage of the β-arylether linkages by neutral sulphite.[2]

A free alcoholic hydroxyl group in the α-position (I), however, is not a requisite for this mode of cleavage. Compounds of the *p*-hydroxybenzyl-alkyl ether type (*e.g.* V) yield the same styrene-β-sulphonic acids (*e.g.* VIII) as do the corresponding *p*-hydroxybenzyl alcohols (*e.g.* IV) (for purification and identification of the reaction products, see experimental section). In the reaction of the *p*-hydroxybenzyl methyl ether V, methanol, and not methane-sulphonic acid (*cf.* Refs. 2 and 3) was formed quantitatively from the methoxyl group attached to the α-carbon atom.

These results show that the strongly nucleophilic sulphite ions attack the benzylic carbon atoms in benzyl ether structures exclusively, suggesting

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* Part II, see Ref. 1.

that methylene quinone residues are common intermediates in the reactions of neutral sulphite with p-hydroxybenzyl alcohol- as well as with p-hydroxy-benzyl ether structures (cf. also Refs. 4 and 5). The methylene quinone residues are expected to react instantly with sulphite ions, producing p-hydroxy-benzyl sulphonic acid structures as intermediates. This early reaction step has now been demonstrated. Treatment of the methylene quinone VI with neutral sulphite at room temperature produced the benzylsulphonic acid VII in nearly quantitative yield.

I   R = H
II   R = side chain of the
        neighbouring unit

III   R = H

IV   R = H
Y   R = CH₃

VI

VIII

VII
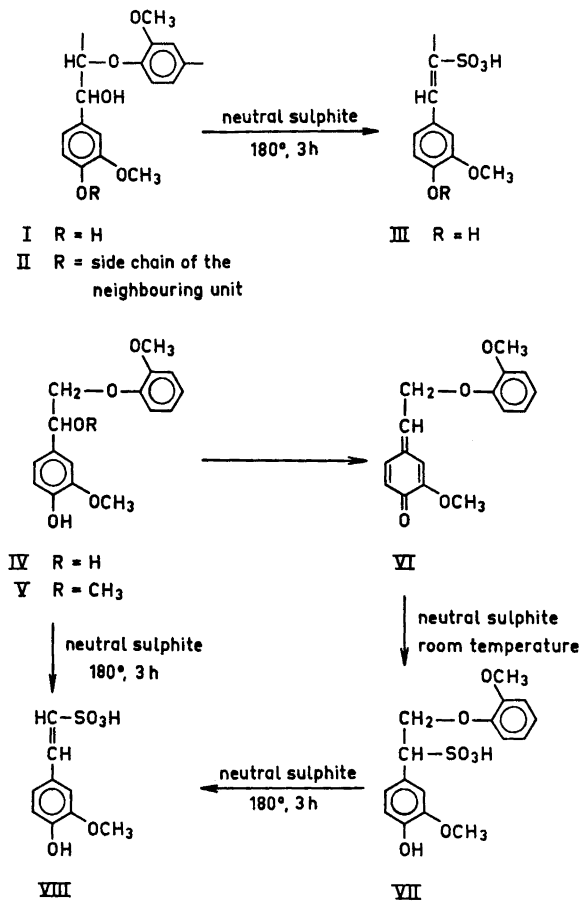
When subjected to the conditions of neutral sulphite pulping (heating with neutral sulphite solution at 180° for 3 h), the benzylsulphonic acid VII was converted into the styrene-β-sulphonic acid VIII in high yield with concomitant liberation of guaiacol. Methylether bonds were also cleaved, to a minor extent, as shown by the formation of methanesulphonic acid [2,3] and

of catechol as minor products. The styrene-β-sulphonic acid VIII was also obtained in a high yield, when the methylene quinone VI was treated with neutral sulphite at room temperature (see above) and the resulting solution, containing the benzylsulphonic acid VII, without isolating the latter, was heated to 180° and kept at this temperature for 3 h.
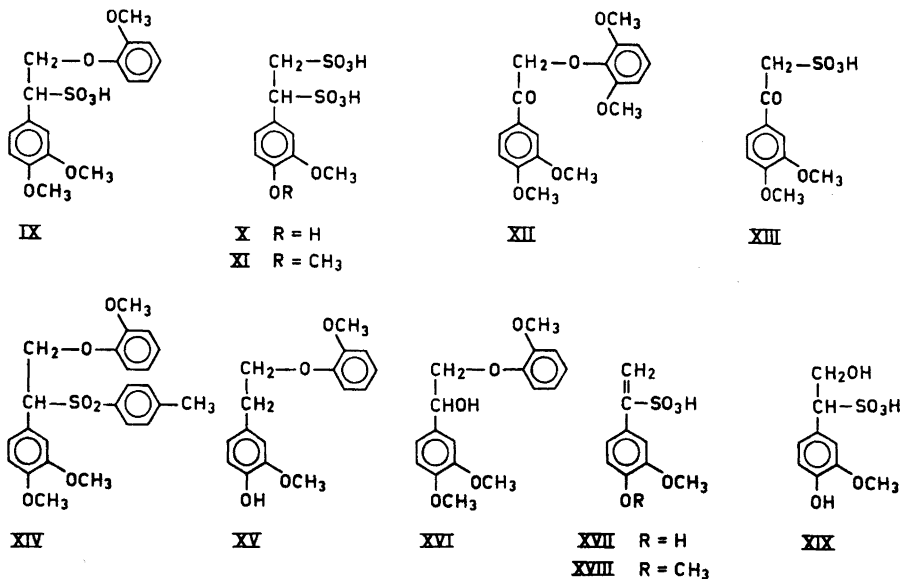
The conversion benzylsulphonic acid (VII)→ styrene-β-sulphonic acid (VIII) may be interpreted in terms of two successive reaction steps. The *first step* involves a nucleophilic attack by the excess sulphite ions present in the cooking liquor on the β-carbon atom resulting in the sulphitolytic fission of the β-aryl ether linkage and in the formation of an α,β-disulphonic acid (X). In fact, the presence of a small amount of the α,β-disulphonic acid X in the reaction mixture obtained from the β-aryl ether IV could be demonstrated. Obviously, this reaction step is of the S_N2 type (*cf.* Ref. 3) and is greatly enhanced, if not rendered possible, by the inductive effect of the strongly electron-attracting sulphonic acid group attached to the α-carbon atom.

In the following the important role of benzylsulphonic acid groups in the sulphitolytic cleavage of β-aryl ether linkages is further elucidated:

1) The cleavage reaction is also given by the non-phenolic benzylsulphonic acid IX which affords the α,β-disulphonic acid XI in a high yield. This confirms the view that fission of a β-aryl ether linkage by neutral sulphite is facilitated by the presence of an adjacent sulphonic acid group. Furthermore, it shows that a free phenolic hydroxyl group *para* to the side chain in the α-sulphonic acids is not necessary for this fission. However, such a phenolic hydroxyl group apparently is essential for the subsequent elimination of the sulphonic acid group from the α-position (second step, see below), as shown by the failure of compound XI to react further. Similarly, this phenolic hydroxyl is necessary for the introduction of a sulphonic acid group into the α-position (see above).

2) The inductive effect of the sulphonic acid group on the sulphitolytic cleavage of the β-aryl ether bond may be substituted by the effect exerted by other electron-withdrawing groups in the α-position, such as carbonyl or sulphone groups. Thus, the 2,6-dimethoxyphenyl ether of 3,4-dimethoxy-β-hydroxy-acetophenone (XII) was quantitatively cleaved yielding a. mixture of 2,6-dimethoxyphenol and its demethylation products, pyrogallol-mono-methyl ether and pyrogallol, as well as the expected phenacyl-β-sulphonic acid (XIII) and methanesulphonic acid.[2,3] The α-sulphone XIV [6] gave a nearly quantitative yield of guaiacol (and some catechol), some methane-sulphonic acid, and other sulphonic acids not identified.

3) In compounds XV and XVI the formation of the intermediary methylene quinone VI and, thus, the introduction of the sulphonic acid group into the α-position is blocked by the absence of an α-hydroxyl- or α-alkoxyl group (XV) and a free phenolic hydroxyl group in *para*-position (XVI), respectively. As expected, these compounds did not afford any noticeable amounts of guaiacol, when treated with neutral sulphite. The starting materials could be recovered in high yields. Some demethylation was indicated by thin-layer chromatography.[2]

IX

CH₂—O—(ring, OCH₃)
CH—SO₃H
(ring, OCH₃, OCH₃)

X R = H
XI R = CH₃

CH₂—SO₃H
CH—SO₃H
(ring, OCH₃, OR)

XII

CH₂—O—(ring, OCH₃, OCH₃)
CO
(ring, OCH₃, OCH₃)

XIII

CH₂—SO₃H
CO
(ring, OCH₃, OCH₃)

XIV

CH₂—O—(ring, OCH₃)
CH—SO₂—(ring)—CH₃
(ring, OCH₃, OCH₃)

XV

CH₂—O—(ring, OCH₃)
CH₂
(ring, OCH₃, OH)

XVI

CH₂—O—(ring, OCH₃)
CHOH
(ring, OCH₃, OCH₃)

XVII R = H
XVIII R = CH₃

CH₂
C—SO₃H
(ring, OCH₃, OR)

XIX

CH₂OH
CH—SO₃H
(ring, OCH₃, OH)

4) The sulphonic acid group in the α-position also facilitates the substitution of the β-aroxy substituent by other (weaker) nucleophiles, e.g. hydroxyl ions. Thus, treatment of the phenolic α-sulphonic acid VII with a borate buffer solution of pH 10 at 180° for 3 h yielded large amounts of guaiacol (about 75 %) and two sulphonic acids, both different from the styrene-β-sulphonic acid VIII. They are tentatively allocated the structures XVII and XIX. On the same treatment with buffer solution the non-phenolic α-sulphonic acid IX afforded guaiacol and 4-vinylveratrole-α-sulphonic acid (XVIII) (80 %), but no styrene-β-sulphonic acid VIII. These results rule out another possible mechanism of styrene-β-sulphonic acid formation, involving neighbouring group participation with the formation of β-sultones [7] as intermediates, ring opening to a methylene quinone sulphurous acid ester and rearrangement with proton elimination to the final styrene-β-sulphonic acid.

The *second step* in the conversion benzylsulphonic acid (VII)→ styrene-β-sulphonic acid (VIII) involves β-elimination. It could be brought about by treating the disulphonic acid X with borate buffer solution of pH 10 at 180° for 3 h. A quantitative conversion into the styrene-β-sulphonic acid VIII was observed. As shown above, the elimination of the sulphonic acid group from the α-position requires the presence of a free phenolic hydroxyl group *para* to the side chain, the non-phenolic disulphonic acid XI being stable under the conditions used. These results indicate that the elimination (like the initial substitution) proceeds *via* a methylene quinone intermediate, the formation of which may be promoted by steric hindrance in the disulphonic acid structure. Proton abstraction from the methylene quinone intermediate by the sulphite ions leads to the styrene-β-sulphonic acid structure. This final step should be facilitated by the electron-withdrawing sulphonic acid

group at the β-carbon atom and by the stabilizing effect of this substituent, as well as that of the aromatic residue at the α-carbon atom, on the resulting olefinic system.
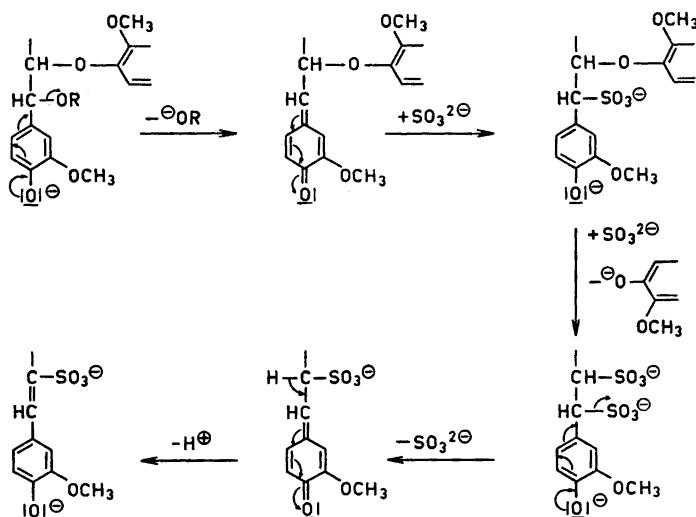
Scheme 1. Mechanism of styrene-β-sulphonic acid formation.

The mechanism of formation of styrene-β-sulphonic acid structures (III) from phenolic structural elements of the β-aryl ether type (I) emerging from these studies is outlined in Scheme 1: A sulphonic acid group is introduced *via* a methylene quinone intermediate and temporarily linked to the α-carbon atom. In this position it facilitates the nucleophilic attack of sulphite ions in the solution on the β-carbon atom, a process which results in the sulphitolytic cleavage of the β-aryl ether linkage and formation of an α,β-disulphonic acid structure. The sulphonic acid group in the α-position is subsequently eliminated, probably *via* a methylene quinone-β-sulphonic acid moiety giving rise to the final styrene-β-sulphonic acid structure.

The results of this work, although strongly supporting the mechanism outlined in Scheme 1, do not exclude a more straight-forward alternative leading directly from the first to the second methylene quinone structure depicted in the Scheme and omitting addition to, and elimination from, the α-position of a sulphite ion. However, the facile formation of the benzylsulphonic acid VII on the one hand, and the detection of the disulphonic acid X in the reaction mixture from compound IV on the other hand, are both in favour of the proposed mechanism.

EXPERIMENTAL

All melting points are corrected. Evaporations were carried out under reduced pressure.

Paper chromatography. The various sulphonic acids, obtained as described below, were investigated by paper chromatography (Whatman No. 3 paper), in some instances

after acetylation of the phenolic hydroxyl group. Mixtures of ethanol-conc. ammonia-water (12:1:3) (system A) and of butanol-acetic acid-pyridine-water (15:3:10:12) (system B) were used as solvents; bromophenol blue served as spray reagent.

Thin-layer chromatography. Sulphonic acid esters, sulphonic acid chlorides, and the other chloroform-ether soluble components were separated on both the analytical and preparative scale by thin-layer chromatography using silica gel HF_{254} (E. Merck A. G., Darmstadt) and, unless otherwise stated, a mixture of chloroform-acetone (9:1) as solvent.

NMR-spectroscopy. The NMR-spectra were run on a Varian A-60 and some spectra on a Perkin-Elmer R-12 spectrometer. Deuterochloroform was used as solvent. Chemical shifts are given in ppm downfield from tetramethylsilane (internal reference).

Model compounds. Of the model compounds used all, except X, XII and XV, had been prepared previously (see Refs. 2, 6 and 8).

Disodium-1-(4-hydroxy-3-methoxyphenyl)-ethane-1,2-disulphonate (sodium salt of X) was prepared following the Strecker procedure [*] with some modifications. To an aqueous solution (25 ml) of $Na_2SO_3 \cdot 7 H_2O$ (12 g), 1-(4-acetoxy-3-methoxyphenyl)-1,2-dibromoethane [10] (5 g) was added and the resulting suspension refluxed for 2 h. After extraction of the unreacted starting material with chloroform, the aqueous solution was evaporated to dryness. The residue was extracted with 80 % ethanol (total 300 ml) to remove excess sodium sulphite and the alcoholic solution evaporated. The new residue was extracted with 90 % ethanol to remove sodium bromide. The sparingly soluble residue contained the sodium salt of the disulphonic acid X and a small amount of sodium sulphite. After cation exchange and saturation with nitrogen, the aqueous solution was neutralized with sodium hydroxide and evaporated to dryness. The crude salt was recrystallized from 80 % ethanol yielding 1.4 g (28 %) pure sodium salt of compound X (paper chromatography, solvent system B).

1-(4-Acetoxy-3-methoxyphenyl)-ethane-1,2-disulphonic acid dimethylester. For further characterisation the disulphonic acid X was converted into its acetylated dimethyl ester. The aqueous solution of the disulphonic acid was neutralized with triethylamine, evaporated to dryness and the residue acetylated with pyridine-acetic anhydride (1:1) at room temperature. After evaporation of the solution, a little water was added to the residue to destroy excess acetic anhydride. The aqueous solution was passed through a column of Dowex 50W−X8 cation exchange resin (H^+-form) and immediately neutralized with silver acetate, filtered and evaporated. The residue was dried *in vacuo* over potassium hydroxide, suspended in acetonitrile (10 ml) and reacted with methyl iodide at room temperature.[11] After the removal of silver iodide by filtration, the solution was evaporated and the residue recrystallized from ethyl acetate-hexane; m.p. 109−111° (Found: C 40.65; H 4.89; O 37.61; S 16.64. $C_{13}H_{18}O_9S_2$ requires: C 40.84; H 4.71; O 37.67; S 16.77). The NMR-spectrum shows 4 singlets at 2.28 ppm (3H), at 3.56 ppm (3H) and 3.76 ppm (3H), and at 3.81 ppm (3H) most likely produced by the protons of the acetyl-, sulphonic ester methoxyl-, and ether methoxyl groups, respectively. The aromatic protons exhibit a sharp signal at 7.07 ppm (3H), the aliphatic protons a multiplet around 4.75 ppm (1H) and a doublet at about 3.98 ppm (2H).

3,4-Dimethoxy-β-(2',6'-dimethoxyphenoxy)-acetophenone (XII) was prepared by reacting 3,4-dimethoxyphenacylbromide (4.0 g) with sodium 2,6-dimethoxyphenolate (6.6 g) in dimethylformamide (50 ml) at room temperature for 1 h; yield 5.3 g=93 %, m.p. after recrystallization from isopropanol 100−103°. (Found: C 65.06; H 6.20; O 28.70; OCH_3 36.03. $C_{18}H_{20}O_6$ requires: C 65.08; H 6.02; O 28.90; OCH_3 37.34). The NMR-spectrum shows three singlets at 3.72 ppm (6H) and 3.85 ppm (6H), attributable to the protons of the four methoxyl groups, and at 5.05 ppm (2H), produced by the protons of the methylene group. The aromatic protons appear as an unresolved multiplet (6H) between 6.35 and 7.75 ppm.

1-(4-Hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-ethane (XV) was prepared by catalytic hydrogenation of compound IV (2 g) dissolved in 93 % acetic acid (165 ml) at room temperature with $PdCl_2$-$BaSO_4$ catalyst (7 g).[12] After filtration and evaporation the residual oil which contained one main component and traces of the starting material was purified by preparative thin-layer chromatography. Compound XV (1.3 g=69 %) was obtained as a colourless oil. In the NMR-spectrum the protons of the two methoxyl groups gave two singlets at 3.82 ppm (3H) and 3.85 ppm (3H), the aromatic protons

an unresolved multiplet at about 6.92 ppm (7H), the aliphatic protons two triplets ($J = 7$ cps) centred at 3.13 (2H) and 4.22 ppm (2H) and the phenolic proton a broad signal at about 5.5 ppm (1H). Compound XV was further characterized by acetylation with acetic anhydride in pyridine and identification of its acetate. *1-(4-Acetoxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-ethane* was obtained as colourless oil. (Found: C 68.54; H 6.31; O 25.26. $C_{18}H_{20}O_5$ requires: C 68.38; H 6.33; O 25.30). The NMR-spectrum is similar to that of compound XV, except that the signal produced by the phenolic proton is missing and an additional singlet appears at 2.27 ppm (3H), due to the protons of the acetyl group.

Cooking liquor. $Na_2S_2O_5$ (0.25 moles) in distilled water (1 l) adjusted to pH 7 with 2 M NaOH.

Cooking conditions. The model compound, suspended in the neutral sulphite solution, was heated in a stainless steel autoclave at 180° for 3 h.

Working-up procedure. The aqueous solution was extracted first with chloroform and then with ether. The combined chloroform-ether extracts were dried (Na_2SO_4), evaporated and the residue was examined by thin-layer chromatography.

The aqueous solution was passed through a column of Dowex 50W−X8 resin (H^+-form), concentrated to about 100 ml and saturated with nitrogen to remove SO_2. After neutralization with barium hydroxide the precipitate of barium sulphate was filtered off and the sulphonic acids were liberated by cation exchange. The aqueous solution was investigated by paper chromatography. In most instances the components of the aqueous solution were converted into acetylated sulphonic acid methyl esters (see compound X, above) or acetylated sulphonic acid chlorides (see compound VIII, section a) below).

Treatments with neutral sulphite solution

a) of compound IV. When the treatment was carried out with 40 ml of neutral sulphite solution/g of compound IV, the final pH value of the cooking liquor was about 10. The resulting styrene-β-sulphonic acid VII was isolated and identified after acetylation and esterification as described for compound X (see above). *trans-4-Acetoxy-3-methoxy-styrene-β-sulphonic acid methyl ester*, m.p. 148−150° after recrystallization from ethylacetate-hexane. (Found: C 50.14; H 5.11; O 33.51; S 11.32. $C_{12}H_{14}O_6S$ requires: C 50.36; H 4.89; O 33.54; S 11.20). In the NMR-spectrum the protons of the sulphonic acid ester methoxyl and of the ether methoxyl exhibit one signal at 3.82 ppm (6H), the acetyl protons a singlet at 2.28 ppm (3H). The olefinic protons give two doublets ($J_{trans} = 15$ cps) centred at 7.55 and 6.63 ppm and the aromatic protons an unresolved multiplet at about 7.07 ppm (3H).

When 80 ml of neutral sulphite solution/g of compound IV was used, the pH value (pH 7) remained constant during the treatment. The water-soluble fraction consisted of the α,β-disulphonic acid X (small amount), in addition to methanesulphonic acid[2] and the styrene-β-sulphonic acid VIII[2] (main product). The latter was converted into its acetate as described for compound X (see above) and neutralized with sodium hydroxide. The sodium salt of the acetylated sulphonic acid VIII was thoroughly dried under reduced pressure and then treated with a mixture consisting of thionyl chloride (10 ml) and dimethylformamide (1 ml) for about 30 min.[13] Methylene chloride (15 ml) was added to the reaction mixture, the precipitated sodium chloride filtered off and the filtrate evaporated. The residue (0.86 g = 86 %) was recrystallized twice from benzene-hexane and gave *trans-4-acetoxy-3-methoxy-styrene-β-sulphonyl chloride* as colourless needles; m.p. 144.5−146.0°. (Found: C 45.55; H 3.48; O 27.65; S 11.02; Cl 12.07. $C_{11}H_{11}O_5SCl$ requires: C 45.46; H 3.78; O 27.52; S 11.03; Cl 12.20). In the NMR-spectrum the olefinic protons exhibit two doublets ($J_{trans} = 15$ cps) centred at 7.70 and 7.17 ppm. The aromatic protons give a rather sharp signal (3H) around 7.13 ppm, the methoxyl protons and the acetyl protons show resonance at 3.87 ppm (3H) and 2.30 ppm (3H), respectively.

b) of compound V. Compound V (0.5 g), prepared as previously described,[6] purified by preparative thin-layer chromatography (solvent: chloroform) and recrystallised from hexane (m.p. 69−70°) (Found: C 67.21; H 6.56; O 26.53; OCH_3 30.42. Calc. for $C_{17}H_{20}O_5$: C 67.12; H 6.57; O 26.30; OCH_3 30.58), was treated with neutral sulphite solution (18 ml). The chloroform-ether extracts contained guaiacol and catechol, but no starting

material. The mixture of water-soluble products consisted of methanesulphonic acid and the styrene-β-sulphonic acid VIII (main product, paper chromatography, solvent systems A and B).

c) of compound VI at room temperature. Compound IV (0.5 g) was converted into the methylene quinone VI.[14] A solution of compound VI in chloroform was shaken with neutral sulphite solution (20 ml) at room temperature. After this treatment the chloroform layer contained only traces of the β-arylether IV and of polymeric material (thin-layer chromatography). In the aqueous layer only the sulphonic acid VII could be detected (paper chromatography). The crude product (0.34 g$=$85 %) was converted into the acetylated methyl ester of the α-sulphonic acid VII following the procedure described above for compound X. After recrystallization from ethanol the product melted at 95$-$96° and gave no depression on admixture of an authentic sample.[2]

d) of compound VI at room temperature and of the resulting compound VII (not isolated) at 180°. Compound IV (1.0 g) was converted into the methylene quinone VI and the latter into the α-sulphonic acid VII as described above (section *c*). The aqueous solution of compound VII (40 ml) obtained was immediately heated to 180° in an autoclave and kept at this temperature for 3 h. After working-up, the chloroform-ether extracts contained guaiacol and catechol, the aqueous solution a small amount of methanesulphonic acid and styrene sulphonic acid VIII (main product) as demonstrated by chromatography. The latter sulphonic acid was converted into the acetylated sulphonic acid chloride as described for the product obtained from compound IV by treatment with neutral sulphite at 180° (see section *a*). The crude product (0.9 g$=$90 %) was recrystallized from benzene-hexane (m.p. 145$-$146°) and found to be identical with that from compound IV (mixed m.p., NMR-spectrum).

e) of compound VII. After treatment of the α-sulphonic acid VII (sodium salt) with neutral sulphite under the usual conditions, only guaiacol and catechol were found in the chloroform-ether extract, and the styrenesulphonic acid VIII and some methanesulphonic acid in the aqueous solution. No starting material (VII) could be detected. The styrenesulphonic acid VIII was isolated in a high yield and characterized by conversion into its acetylated chloride as described in section *a*). The products were identical (m.p. and mixed m.p.).

f) of compound IX. The non-phenolic α-sulphonic acid IX (0.5 g sodium salt) prepared by acidic sulphonation [2] of compound XVI, on neutral sulphite treatment, yielded guaiacol and catechol in the chloroform-ether soluble fraction, as well as methane sulphonic acid and an unknown sulphonic acid in the aqueous solution. Esterification following the procedure described previously [2] and purification by preparative thin-layer chromatography gave *1-(3,4-dimethoxyphenyl)-ethane-1,2-disulphonic acid dimethylester* (dimethylester of compound XI) (0.37 g$=$82 %), m.p. 118$-$120° after recrystallization from ethanol. (Found: C 40.62; H 5.46; O 35.79; S 17.82. $C_{12}H_{18}O_8S_2$ requires: C 40.68; H 5.08; O 36.13; S 18.10). The NMR-spectrum shows three singlets at 3.87 ppm (6H), 3.73 ppm (3H) and 3.62 ppm (3H) attributable to the protons of the ether methoxyl- and α- and β-sulphonic ester methoxyl groups, respectively. The aromatic protons and the aliphatic protons exhibit unresolved multiplets around 6.97 ppm (3H), 4.68 ppm (1H) and 4.00 ppm (2H), respectively.

g) of compound XII. Compound XII yielded 2,6-dimethoxyphenol, pyrogallolmonomethyl ether and pyrogallol as chloroform-ether soluble compounds. No starting material could be detected. Methanesulphonic acid, 3,4-dimethoxyphenacyl sulphonic acid (XIII) and traces of a third sulphonic acid, probably a demethylation product of compound XIII, were shown to be present in the aqueous solution. The two former sulphonic acids were identified by paper chromatography (solvent systems A and B) and comparison with authentic samples.

h) of compound XIV. Compound XIV, prepared according to Ref. 6, gave guaiacol and catechol but no starting material in the chloroform-ether soluble fraction. Paper chromatography of the aqueous solution revealed the presence of methanesulphonic acid and of several other sulphonic acids which were not characterized.

i) of compound XV. After treatment of compound XV with neutral sulphite the chloroform-ether extract contained two components, the dominating one being the starting material. In the aqueous solution only a small amount of methanesulphonic acid was found.

Table 1. Treatments with neutral sulphite solution at 180° C for 3 h.

Starting material	Reaction products		Remarks
	CHCl$_3$- ether soluble	water soluble	
IV	G^a, C^a	MS^a, VIII	final pH 10
IV	G, C	MS, VIII, X(traces)	final pH 7
V	G, C	MS, VIII	
VI	IV (traces), polymeric material	VII	treatment at room temperature
VII	G, C	MS, VIII	starting material prepared from VI and not isolated
VII	G, C	MS, VIII	
IX	G, C	MS, XI	
XII	2,6-dimethoxyphenol, pyrogallolmono-methyl ether, pyrogallol	MS, XIII unknown acid (traces)	
XIV	G, C	MS, other sulphonic acids (not identified)	
XV	starting material	MS (small amount)	

^{a} G = guaiacol, C = catechol, MS = methanesulphonic acid.

Table 2. Treatments with borate buffer solution of pH 10 at 180°C for 3 h.

Starting material	Reaction products	
	CHCl$_3$-ether soluble	water soluble
VII	G^b	starting material, traces of XVII^a and XIX^a
IX	G	XVIII
X	—	VIII

^{a} structure not settled. ^{b} G = guaiacol.

Treatments   with   borate   buffer   solution   at   pH   10

a) of compound VII. Compound VII (0.5 g sodium salt) was treated with a borate buffer solution (pH 10) at 180° for 3 h. In the chloroform-ether extract guaiacol was the main component (0.12 g = 75 %). The aqueous solution contained the starting sulphonic acid VII and two other sulphonic acids different from compound VIII, probably having the structures XVII (*cf.* b, below) and XIX (paper chromatography).

b) of compound IX. After treatment with the borate buffer solution, the sodium salt of compound IX (0.5 g) gave a chloroform-ether extract containing only guaiacol. In the aqueous solution only one sulphonic acid, not identical with the starting material, was found. Esterification (see Ref. 2) and purification of the methyl ester by preparative thin-layer chromatography afforded *1-(3,4-dimethoxyphenyl)-ethene-1-sulphonic acid methyl ester* (methyl ester of compound XVIII) (0.27 g = 81 %); m.p. 34—36° after recrystallization from ligroin (Found: C 51.26; H 5.25; O 31.02; S 12.32. $C_{11}H_{14}O_5S$ requires: C 51.17; H 5.42; O 30.98; S 12.42). The NMR-spectrum shows two singlets at 3.75 ppm (3H) and 3.90 ppm (6H), due to the protons of the sulphonic ester methoxyl and the ether methoxyl groups, respectively. The geminal protons appear at 6.08 (1H) and 6.42 (1H) ppm and the aromatic protons as an unresolved multiplet (3H) around 7.02 ppm.

c) of compound X. The sodium salt of compound X (0.5 g) was similarly treated with the buffer solution. The resulting aqueous solution contained only one sulphonic acid which was converted into its acetylated methyl ester as described for compound X (see above). A nearly quantitative yield (0.47 g) of the *trans*-4-acetoxy-3-methoxy-styrene-β-sulphonic acid methyl ester was obtained which was shown to be identical with the product isolated after neutral sulphite treatment of compound IV (see above).

The results of the treatments with neutral sulphite solution and with borate buffer solution are summarized in Tables 1 and 2.

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