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# The Reactions of Lignin during Sulphate Cooking

## Part VIII.* The Mechanism of Splitting of β-Arylether Bonds in Phenolic Units by White Liquor**

JOSEF GIERER and LEIF-ÅKE SMEDMAN

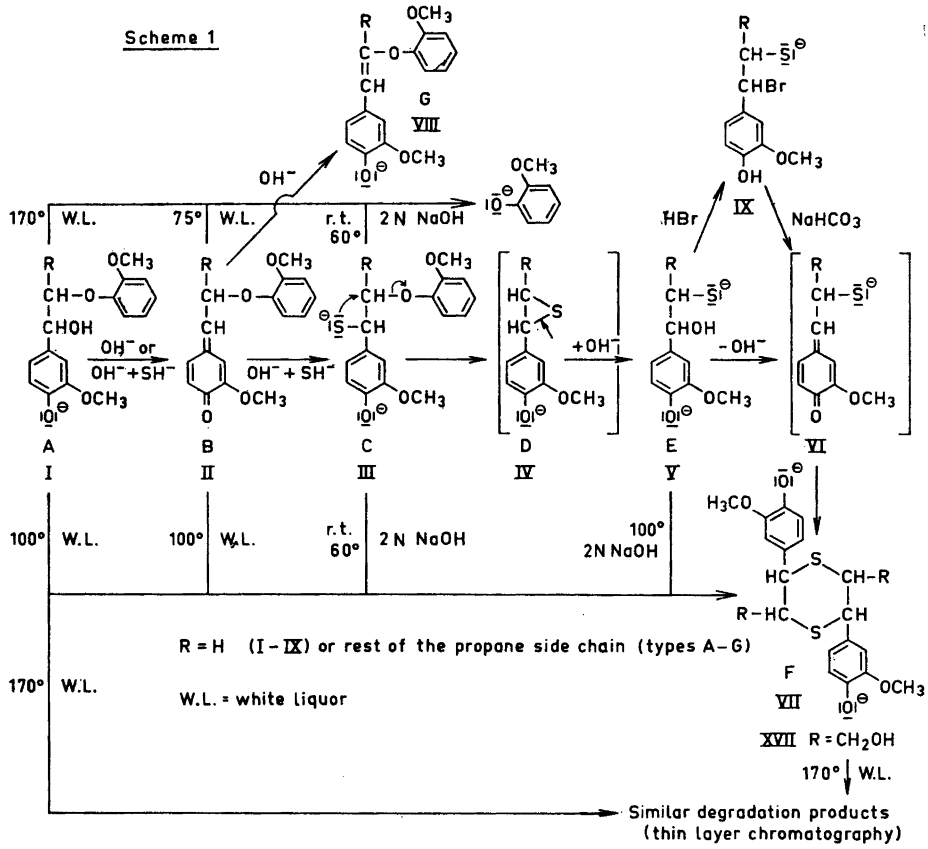
*Swedish Forest Products Research Laboratory, Department of Wood Chemistry, Stockholm, Sweden*

The splitting of β-arylether bonds in phenolic lignin units (type A, scheme 1) by white liquor has been studied with appropriate model compounds and with some of the intermediates expected to be formed from these model compounds during the splitting reaction. The route for the synthesis of the intermediates (scheme 2) and their behaviour towards white liquor and 2 N sodium hydroxide support the mechanism suggested recently [1] and outlined in scheme 1. This mechanism includes the incorporation of sulfhydryl groups into lignin and explains the important function of these groups in enhancing the alkaline cleavage of arylether linkages. In terms of the results obtained it is possible to interpret the favourable effect of the inorganic sulphide present in white liquor on the dissolution of lignin during sulphate cooking.

Recent model experiments have shown that β-arylether bonds in phenolic lignin units (type A) can be split by 2 N sodium hydroxide at 170° to the extent of about 30%, whereas this type of bonds undergoes practically complete fission when exposed to white liquor ** under otherwise identical conditions [1] (*cf.* also Ref. 2). In order to explain this striking difference in the behaviour of β-arylether linkages located in phenolic lignin units towards the two splitting reagents, two different pathways of splitting were proposed.[1] The partial splitting by the action of 2 N sodium hydroxide was considered to proceed, at least partly, *via* the corresponding methylene quinone-(B) and enolether-(G) structures. An example of the latter type of compound (VIII) has been isolated and identified in previous model experiments.[3] The almost complete cleavage brought about by white liquor was suggested to take essentially the course described in scheme 1.

* Part VII, see Ref. 14.

** The term "white liquor", used throughout this work, refers to a solution of NaOH (3.5 g) and $Na_2S \cdot 9\ H_2O$ (3.1 g) in water (100 ml).



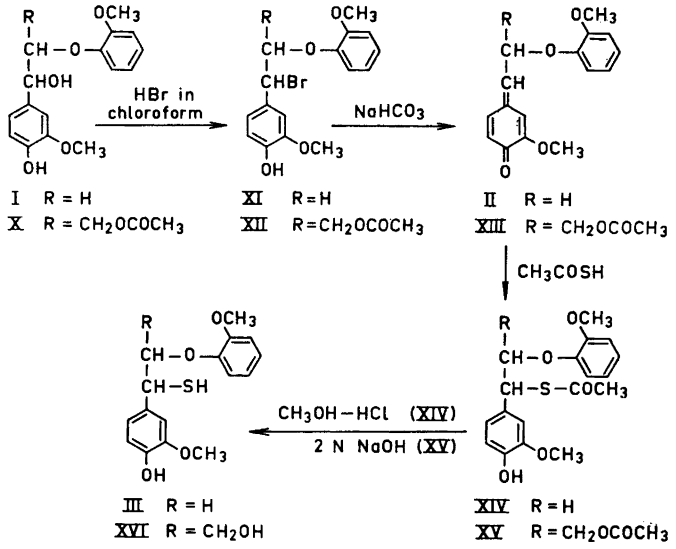

The present work deals with an attempt to confirm this mechanism of splitting. Some of the intermediates proposed in scheme 1 were synthesised and their behaviour towards white liquor and/or towards 2 N sodium hydroxide was studied.

## RESULTS AND DISCUSSION

The convenient route of converting hydroxyl compounds into sulfhydryl compounds, *i.e.* esterification of the hydroxyl group with toluene-*p*-sulphonyl chloride, followed by exchange of the toluene-*p*-sulphonyloxy group for a thioacetyl group and its subsequent hydrolysis,[4,5] could not be followed in the preparation of benzylthiols of type C, since the tosylation of the benzylalcoholic hydroxyl group in β-arylethers (type A) is difficult to accomplish. Therefore, another route of synthesis was tried (scheme 2).

A β-arylether of the *p*-hydroxy-benzylalcohol type (*e.g.* I or X) was treated with hydrogen bromide in ethanol-free chloroform and the resulting *p*-hydroxy-benzylbromide (XI or XII) was converted into the methylene quinone (II

Scheme 2




or XIII) by shaking the chloroform solution of the bromide with an aqueous solution of sodium hydrogen carbonate.[6-8] The methylene quinone readily added thioacetic acid to yield the corresponding *p*-hydroxy-benzylthioacetate (XIV or XV). From the thioacetate the free *p*-hydroxy-benzylthiol (III or XVI) was prepared by acidic or mild alkaline hydrolysis of the *S*-acetyl bond.

Apart from leading to good yields of *p*-hydroxy-benzylthiols (C) this route of synthesis makes easily available *p*-methoxy-benzylthiols and *p*-hydroxy-benzyl-alkylthioethers.[9] Moreover, it includes the facile addition of dissociated sulfhydryl groups (R—$\overline{S}|\ominus$) to methylene quinone structures. This reaction illustrates a possible way of incorporation of sulphur into lignin during sulphate cooking and constitutes an introductory step in the suggested course of splitting (B→C, see scheme 1).

The compounds prepared can only be regarded as intermediates if they react with white liquor with at least the same ease as is observed for the corresponding starting compound (phenolic *β*-arylether of type A). It will be shown below that all the intermediates prepared fulfil this prerequisite.

Thus, the guaiacylether bond in the methylene quinone II (scheme 1) was split by white liquor at 75° within half an hour to an extent of 52—56 %, whereas appreciable cleavage of the guaiacylether bond in the parent *p*-hydroxy-benzylalcohol (I) required temperatures of between 150 and 170 °.[1] Both compounds (I[1] and II) only gave negligible amounts of the enolether VIII when heated with white liquor at 170°. Conversely, the guaiacylether bond in both compounds was only split to a minor extent and the enolether VIII was formed as the main product when the compounds were heated with 2 N sodium

hydroxide at 170°. Thus, the behaviour of the methylene quinone II towards white liquor and towards 2 N sodium hydroxide resembled to a great extent the behaviour of the *p*-hydroxy-benzylalcohol I towards the same splitting reagents. The only difference observed was the greater sensitivity of the guaiacylether bond in the former compound towards white liquor. These results are compatible with the assumption that methylene quinone structures (B) constitute intermediates in the reactions of the *β*-arylether structures in phenolic units (A) with both white liquor and 2 N sodium hydroxide.

The guaiacylether bond in the intermediate following the methylene quinone II, *i.e.* in the *p*-hydroxy-benzylthiol III, was split with still greater ease. Treatment of compound III with 2 N sodium hydroxide at 60° for 15 min or at room temperature for 6 h afforded a quantitative yield of guaiacol. As in the alkaline splitting of guiacylethers of thioglycerols [5] this smooth cleavage of the guaiacylether bond may be explained in terms of an intramolecular nucleophilic displacement of the aroxyl anion by the neighbouring mercaptide anion involving the intermediary formation of an episulphide (IV, scheme 1) [1] (*cf.* also Ref. 10).

Experimental support for this mechanism has now been furnished. After treatment of the *p*-hydroxy-benzylthioacetate XIV with 2 N sodium hydroxide at room temperature for 12 h followed by removal of a small amount of a precipitate (see below) and of the liberated guaiacol an amorphous product was isolated in good yield. Attempts to crystallise it by treatment with various solvents or to purify it by preparative thin-layer chromatography were unsuccessful. On the basis of chromatographic behaviour, sulphur content, colour reactions and its facile conversion into compound VII (see below) structure V is tentatively proposed.

The yield (about 5 %) of the substance which precipitated directly from the alkaline reaction mixture increased to 77 % when the alkaline treatment of compound XIV was carried out at 100° for 2 h. Good yields were also obtained when the free *p*-hydroxy-benzylthiol III or the crude compound V was treated with 2 N sodium hydroxide under similar conditions (see experimental section).

The substance was assumed to be a disodium salt. It was converted into the free phenolic form which melted at 250—250.5°. The analyses of the latter agreed with the formula $[C_8H_7OS(OCH_3)]_n$, where $n$ was found to be equal to 2(molecular weight determination). Acetylation with acetic anhydride-pyridine afforded a diacetate melting at 268—269°. The substance, therefore, is considered to be a dithiane (VII) * formed from the intermediary unstable monothio-ethyleneglycol derivative V by conversion into the methylene quinone VI, followed by dimerisation of the latter (scheme 1).

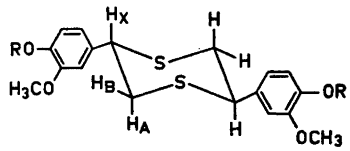
The PMR spectra of solutions of the phenolic substance and its diacetate in deuterated dimethylsulphoxide with tetramethylsilane as internal reference (Table 1, p. 1107) were in good agreement with the structures of 2,5-di-(4-hydroxy-3-methoxy-phenyl)-1,4-dithiane (VII) and 2,5-di-(4-acetoxy-3-meth-

* *Note added in proof.* In a comparative study of the sulphonation and the sulphidation of compound I, dithiane VII was also obtained by K. Kratzl and J. Spona, University of Vienna (personal communication).

*Table 1.* Proton chemical shifts ($\delta$-values in ppm) and spin coupling constants (c/s) in 2,5-di-(4-hydroxy-3-methoxy-phenyl)-1,4-dithiane (VII) and in 2,5-di-(4-acetoxy-3-methoxy-phenyl)-1,4-dithiane (VII a).

| Compound | OAc | OMe | Arom. | $H_B$ | $H_A$ | $H_X$ | Spin couplings (c/s) |
|---|---|---|---|---|---|---|---|
| VII | — | 3.80 | 6.89 | 2.95 | 3.48 | 4.15 | $J_{AX}=10.7$, $J_{BX}=2.5$ $J_{AB}=13.3$ |
| VIIa | 2.21 | 3.80 | 7.15 | 3.05 | 3.54 | 4.28 | $J_{AX}=10.9$, $J_{BX}=2.5$ $J_{AB}=13.3$ |

oxy-phenyl)-1,4-dithiane (VII a), respectively. A comparison of the PMR spectra with those of *cis-* and *trans*-2,5-diphenyl-1,4-dioxan [11] and of *trans*-2,5-di-(4-acetoxy-3-methoxy-phenyl)-1,4-dioxan [12] revealed that a *trans*-arrangement of the guaiacyl nuclei in compounds VII and VIIa (Fig.1) is the more probable one.




VII R = H
VIIa R = $CH_3CO$

*Fig. 1.*

The view that the dithiane VII is formed *via* the corresponding methylene quinone VI is supported by the finding that compound VII is also obtained by converting the crude hydroxythiol V into the bromothiol IX and shaking a chloroform solution of the latter with an aqueous solution of sodium hydrogen carbonate (see scheme 1). From the chloroform layer the dithiane VII was isolated (yield 63.5 %), indicating that the intermediary methylene quinone VI had dimerised spontaneously. The course of this reaction also supports the structure of the parent hydroxythiol V, since the isomeric form having the thiol group in $\alpha$- and the hydroxyl group in $\beta$-position would be expected to yield the corresponding dioxan (VII, O instead of S), m.p. 213—214°. The latter compound was recently obtained by treating (4-hydroxy-3-methoxy-phenyl)-ethyleneglycol or 1-(4-hydroxy-3-methoxy-phenyl)-2-(hydroxy)-ethyl-*p*-tolylsulphone with 2 N sodium hydroxide at 100°.[12] Furthermore, the formation of the hydroxythiol V from the aroxythiol III is in good agreement with the view that the cleavage of the $\beta$-arylether bond involves an episulphide intermediate (IV), hydrolytic opening of the latter resulting in the rearrangement of an $\alpha$-thiol (III) to a $\beta$-thiol (V).

The mechanism of splitting outlined in scheme 1 requires that the dithiane VII should be formed not only when the aroxythiol III or the resulting hydroxythiol V is treated with 2 N sodium hydroxide, but also when the starting $\beta$-guaiacylether I or the intermediate methylene quinone II is reacted with

white liquor. In fact, heating of the phenolic guaiacylether I (4 days) and of the methylene quinone II (30 min) with white liquor at 100° gave the dithiane VII in yields of 32 % and 72 %, respectively.

When subjected to the conditions of sulphate cooking, *i.e.* heating with white liquor at 170° for 2 h, the dithiane VII (S = 17.61 %) was converted into a mixture of products containing only 5.36 % sulphur. Thus, considerable elimination of sulphur (70 %) had taken place during this treatment, resulting in a sulphur content comparable to that of the mixture of degradation products formed on sulphate cooking of the phenolic β-guaiacylether I (S = 7.19 %). Furthermore, the chromatographic patterns (thin-layer chromatography) of the two degradation mixtures were similar.

It has not yet been decided whether the dithiane structures (F) actually are intermediates in the reaction at 170° or stabilisation products accumulating only at lower reaction temperatures. The sulphur content and the chromatographic behaviour of the mixture of degradation products obtained from compound VII do not rule out the former alternative. Moreover, the elimination of sulphur from compound VII during treatment with white liquor at 170° reflects the desulphuration of lignin during the later stages of sulphate cooking.[13]

The sulphur containing model compounds having a complete $C_3$ side-chain behave analogously. The route of synthesis for the *p*-hydroxy-benzylthiol XVI (scheme 2) was essentially the same as for compound III and the guaiacylether bond in compounds XVI and III showed a similar sensitivity towards 2 N sodium hydroxide. After treatment of compound XV with 2 N sodium hydroxide at 100° the corresponding dithiane (XVII, scheme 1) was isolated and characterised by analysis and conversion into its tetraacetate.

The model studies described may provide a possible explanation for the role of sulphur displayed in the course of sulphate cooking. They illustrate a pathway for the temporary incorporation of sulphur by the addition of sulphide ions to methylene quinone structures formed in lignin by the action of alkali. The studies also elucidate the function of sulphide ions in facilitating the alkaline splitting of β-arylether bonds and indicate the partial elimination of sulphur after this splitting reaction. There may be additional ways for the incorporation of sulphur and further degradation reactions favoured by the presence of sulphide ions in the alkaline cooking liquor. However, phenolic structures containing β-arylether bonds (type A) are comparatively abundant during sulphate cooking (*cf.* Ref. 14) and, therefore, the view seems to be justified that the main function of the sulphide ions is to be found in the sequence of reactions depicted in scheme 1.

## EXPERIMENTAL

All melting points are corrected. Evaporations were carried out *in vacuo*. Preparative thin-layer chromatography was carried out on silica gel $HF_{254}$.[15] This allowed the localisation of the zones using ultraviolet. Chloroform was used as solvent.

The proton magnetic resonance (PMR) spectra were recorded at 60 Mc/s on a Varian A60 spectrometer. The shifts are reported as δ-values in ppm.

## Preparation of proposed intermediates

*1-S-Acetyl-1-(4-hydroxy-3-methoxy-phenyl)-2-O-(2-methoxy-phenyl)-1-monothioethyleneglycol (XIV).* 1-(4-Hydroxy-3-methoxy-phenyl)-2-*O*-(2-methoxy-phenyl)-ethyleneglycol (I) (5.5 g) was dissolved in chloroform (250 ml) which had been freed from ethanol. Dry hydrogen bromide was passed through the solution until it became turbid and the treatment was continued for another 30 min. At the end of the reaction time the chloroform solution containing the *p*-hydroxy-benzylbromide XI was vigorously shaken with an equal volume of a saturated aqueous solution of sodium hydrogen carbonate. The colour of the chloroform layer turned intensely yellow indicating the conversion of the *p*-hydroxy-benzylbromide XI into the methylene quinone II. After separation from the aqueous layer, sodium sulphate and subsequently an excess of thioacetic acid were added to the chloroform solution which rapidly decolourised. The reaction mixture was kept at room temperature over-night. Evaporation of the solvent afforded a slightly yellow solid (6.5 g) which was recrystallised from isopropanol or from di-isopropylether. A voluminous precipitate of colourless needles was obtained (yield 5.5 g, 84 %), m.p. 131–132°. (Found: C 62.19; H 5.74; O 23.10; S 8.96. $C_{18}H_{20}O_5S$ requires: C 62.05; H 5.79; O 22.96; S 9.20).

The PMR spectrum of XIV (in carbon tetrachloride at 90° and with dimethylsulphoxide as internal reference) gave the following results: three acetyl protons $\delta = 2.40$, six methoxyl protons $\delta = 3.88$ and 3.95, two methylene protons (a doublet) $\delta = 4.42$, one methine proton (a triplet) $\delta = 5.02$ and seven aromatic protons $\delta =$ about 7.00. The coupling constant ($J_{\alpha\beta}$) between the protons of the α- and β-carbon atom of the aliphatic side chain was $J_{\alpha\beta} = 6.0$ c/s.

*1-(4-Hydroxy-3-methoxy-phenyl)-2-O-(2-methoxy-phenyl)-1-monothioethyleneglycol (III)* was prepared by hydrolysis of 1-*S*-acetyl-1-(4-hydroxy-3-methoxy-phenyl)-2-*O*-(2-methoxy-phenyl)-1-monothioethyleneglycol (XIV) (2.0 g) with 2 N methanolic hydrogen chloride (200 ml) in an atmosphere of nitrogen at the boiling point (30–45 min). When the reaction was complete (thin-layer chromatography), the solution was poured into an equal volume of ice-water. The free thiol (III) was extracted with chloroform and the chloroform solution was washed with water and dried with sodium sulphate. Evaporation yielded a colourless oil (1.7 g, 97 %) which crystallised after having been kept in a refrigerator for several days. The substance could be recrystallised from ether-light petroleum at −70° giving needles, m.p. 30–33°. (Found: C 62.70; H 6.15; O 20.78; S 10.48. $C_{16}H_{18}O_4S$ requires: C 62.72; H 5.92; O 20.89; S 10.47).

Comparison of the PMR spectrum of the *p*-hydroxy-benzylthiol (III) with that of the *S*-acetate (XIV) showed that the methine proton had moved up-fields causing coincidence of the methine and the two methylene protons with the formation of an unresolved multiplet ($\delta$ about 4.20). Six methoxylic $\delta = 3.67$ and 3.70, one thiolic (a doublet) $\delta = 2.47$ ($J = 4$ c/s) and one phenolic proton $\delta = 5.95$ were observed. The latter disappeared when III was treated with deuterated water.

*3-O-Acetyl-1-(4-hydroxy-3-methoxy-phenyl)-2-O-(2-methoxy-phenyl)-glycerol (X).* 3-Acetoxy-1-(4-benzyloxy-3-methoxy-phenyl)-2-(2-methoxy-phenoxy)-propan-1-on (2.5 g) was suspended in methanol (40 ml) and catalytically hydrogenated (Pd on charcoal).[16] After removal of the catalyst and the solvent a colourless viscous oil was obtained. Yield: 2.0 g, 99 %. (Found: C 63.00; H 6.17; O 30.66; $CH_3CO$ 10.67. Calc. for $C_{19}H_{22}O_7$: C 62.97; H 6.12; O 30.91; $CH_3CO$ 11.88).

*3-O-Acetyl-1-S-acetyl-1-(4-hydroxy-3-methoxy-phenyl)-2-O-(2-methoxy-phenyl)-1-monothioglycerol (XV)* was prepared from 3-*O*-acetyl-1-(4-hydroxy-3-methoxy-phenyl)-2-*O*-(2-methoxy-phenyl)-glycerol (X) (4.9 g) using essentially the same method as described for 1-*S*-acetyl-1-(4-hydroxy-3-methoxy-phenyl)-2-*O*-(2-methoxy-phenyl)-1-monothioethyleneglycol (XIV, see above). After evaporation of the chloroform the thioacetate (XV) was obtained as a yellowish oil. Purification by means of preparative thin-layer chromatography yielded a colourless oil (4.5 g, 80 %) which exhibited two strong peaks in the carbonyl region of the infrared spectrum, one at 1685 $cm^{-1}$, due to *S*-acetyl [17] and the other at 1735 $cm^{-1}$, due to *O*-acetyl.[17] (Found: C 59.72; H 5.77; O 26.55; S 7.46; $CH_3CO$ 20.06. $C_{21}H_{24}O_7S$ requires: C 59.98; H 5.75; O 26.64; S 7.63; $CH_3CO$ 20.47).

*1-(4-Hydroxy-3-methoxy-phenyl)-2-O-(2-methoxy-phenyl)-1-monothioglycerol (XVI)* was obtained as a slightly yellow oil (0.76 g) by treating 3-*O*-acetyl-1-*S*-acetyl-1-(4-

hydroxy-3-methoxy-phenyl)-2-*O*-(2-methoxy-phenyl)-1-monothioglycerol (XV) (1.9 g) with 2 N sodium hydroxide at room temperature in an atmosphere of nitrogen for 4 h. The crude product was purified by preparative thin-layer chromatography to give a colourless oil (0.53 g, 35 %). The infrared spectrum did not show any band in the carbonyl region but a small peak at 2550 $cm^{-1}$, due to the liberated sulfhydryl group.[17] (Found: C 60.60; H 6.49; O 23.66; S 9.67. $C_{17}H_{20}O_5S$ requires: C 60.70; H 5.99; O 23.78; S 9.53).

## Reactions of proposed intermediates with white liquor and/or with 2 N sodium hydroxide

*Liberation of guaiacol. (a) From methylene quinone II.* Solutions of the methylene quinone II (100—110 mg) in chloroform (10 ml) were prepared from compound I as described in the preparative section and dropped into stirred white liquor (25 ml) or 2 N sodium hydroxide (25 ml) at 75° during a 10 min period. When the addition was complete, the solutions were stirred for another 20 min and then neutralised with carbon dioxide and extracted with chloroform. The guaiacol content of the chloroform extracts was determined by gas-liquid chromatography following the procedure published recently [1] with the exception that the temperature of the injection block was descreased from 250° to 200°. The values obtained were corrected for the small amounts of guaiacol formed during the preparation of the methylene quinone II. Duplicate experiments with both white liquor and 2 N sodium hydroxide were performed using two different preparations of the methylene quinone. The following percentages of guaiacol split off were found: with white liquor 56 and 52, and with 2 N sodium hydroxide 3 and 6. When the reaction mixtures, obtained after treatment of methylene quinone II with 2 N sodium hydroxide at 75°, were heated to 170° for 2 h, the enolether VIII was formed as the main product (thin-layer chromatography) (*cf.* also alkali-treatment of compound I).[1] Heating of the reaction mixture to 170° for 2 h after treatment of methylene quinone II with white liquor gave only small amounts of compound VIII.

(*b*) *From* p-*hydroxy-benzylthiol III and its* S-*acetate XIV.* Samples of the free thiol III (100 mg) and its *S*-acetate XIV (100 mg) were treated with 2 N sodium hydroxide at room temperature and at 60° for different lengths of time and the reaction mixtures were worked up as described above. Gas chromatographic determination of the proportions of guaiacol split off revealed that the cleavage of the guaiacylether bond in III and in XIV by the action of 2 N sodium hydroxide at room temperature was complete after 6 h, whereas quantitative splitting of this bond at 60° was observed after 15 min.

Similar results were obtained after treatment of the *p*-hydroxy-benzylthiol XVI and its diacetate XV with 2 N sodium hydroxide at room temperature and at 100° (see also formation of dithiane XVII, below).

*Formation of dithiane VII.* (1) *From* p-*hydroxy-benzylthioacetate XIV. (a) at room temperature.* A suspension of compound XIV (3.8 g) in 2 N sodium hydroxide (150 ml) was stirred at room temperature in an atmosphere of nitrogen. In the course of some minutes a clear solution was obtained and after 12 h a small amount (0.1 g) of a white solid had deposited. This was filtered off and characterised as described for the precipitate obtained from compound V after treatment with 2 N sodium hydroxide at 100° (see below).

The filtrate was neutralised with carbon dioxide, extracted with chloroform, and the concentrated chloroform extract was fractionated by column chromatography on silica gel (Mallinckrodt, 100 mesh). The elution was started with chloroform to give guaiacol and several smaller fractions which were not characterised. Further elution with chloroform containing increasing amounts (0—5 %) of ethanol gave a fraction containing the main component. Evaporation of the solvent yielded a yellowish oil (1.6 g, 73.5 %) which was purified by preparative thin-layer chromatography. Attempts to remove the last impurities by thin-layer chromatography and precipitation from different combinations of solvents were not successful. The chromatographic behaviour, the sulphur content (16.32 %, calc. 16.01 %) and the colour reactions with 2,6-dibromo-quinone-4-chloroimide and with 2,3,5-triphenyltetrazolium chloride were compatible with the assumption that the product was a 4-hydroxy-3-methoxy-phenyl-monothioethyleneglycol. Support for structure V, *1-(4-hydroxy-3-methoxy-phenyl)-2-monothioethyleneglycol*, was provided by treating the product (100 mg) with 2 N sodium hydroxide (5 ml) at 100° for 3 h. A colour-

less crystalline precipitate formed. This was filtered off, washed with water, suspended in 2 N hydrochloric acid and the suspension was stirred at room temperature over-night. After filtration the precipitate was recrystallised from ethanol to yield colourless prisms of *2,5-di-(4-hydroxy-3-methoxy-phenyl)-1,4-dithiane (VII)* (45 mg), m.p. 250–250.5°. An additional amount (29 mg, total yield 82 %) of compound VII could be isolated from the alkaline filtrate by acidifying (hydrochloric acid) and extracting with chloroform. (Found: C 59.30; H 5.73; O 17.63; S 17.62. $C_{18}H_{20}O_4S_2$ requires: C 59.34; H 5.49; O 17.57; S 17.61). Acetylation of compound VII with acetic anhydride and pyridine and recrystallisation of the crude acetylation product from chloroform-hexane yielded *2,5-di-(4-acetoxy-3-methoxy-phenyl)-1,4-dithiane (VII a)*, m.p. 267.5–268.5°. (Found: C 58.86; H 5.27; O 21.24; S 14.17; $CH_3CO$ 18.57. $C_{22}H_{24}O_6S_2$ requires: C 58.93; H 5.35; O 21.41; S 14.30; $CH_3CO$ 19.41). (for PMR spectra, see Table 1).

The crude monothioethyleneglycol derivative V (60 mg) could also be converted into the dithiane VII by treatment with hydrogen bromide in chloroform and shaking the chloroform solution of the resulting bromothiol IX with a saturated aqueous solution of sodium hydrogencarbonate (yield 35 mg, 63.5 %), m.p. 250—250.5°, undepressed after admixture of dithiane VII prepared from compound III by the action of 2 N sodium hydroxide.

*(b) at 100°.* Compound XIV (1.0 g) was dissolved in 2 N sodium hydroxide (5 ml). The solution was heated to 100° in an atmosphere of nitrogen and kept at this temperature for 2 h. After a few minutes a white crystalline substance started to precipitate, the amount rapidly increasing during the first hour of heating. It was filtered off, converted into the free phenolic form and purified as described for the product obtained from compound V (see above). M.p. 249.5–250.5°, mixed m.p. 249–250°, PMR-spectrum and analytical values proved it to be identical with compound VII (yield 403 mg, 77 %).

2) *From* p-*hydroxy-benzylthiol III. (a) at room temperature.* Compound III (150 mg) was dissolved in 2 N sodium hydroxide (10 ml) and the solution was kept at room temperature in an atmosphere of nitrogen for 6 h. Neutralisation with carbon dioxide gave a white precipitate which was centrifuged off, washed with water and dried. Yield: 100 mg, 100 %. Conversion into the phenolic compound VII (see above) and recrystallisation from ethanol yielded colourless prisms (15 mg), m.p. 246–248°, mixed m.p. with compound VII obtained from the *S*-acetate XIV (see above) showed no depression.

*(b) at 60°.* Compound III (90 mg) was treated with 2 N sodium hydroxide (10 ml) at 60° in an atmosphere of nitrogen for half an hour and the reaction mixture worked up as described above to yield 25 mg (47 %) of compound VII, m.p. 246–248°.

3) *from methylene quinone II.* A chloroform solution (70 ml) of compound II, prepared from compound I (1 g) as described above, was dropped into vigorously stirred white liquor (200 ml) at 100° during a 15 minute period. The chloroform solution was added at such a rate that the solvent immediately evaporated. The reaction mixture was kept at 100° for 15 min after the addition had been completed. A dark-coloured product (170 mg) precipitated and was found to be the crude sodium salt of the dithiane VII. From the alkaline mother liquor an additional amount (300 mg) of compound VII could be isolated after neutralisation with carbon dioxide and recrystallisation from ethanol. M.p. 250–250.5° and mixed m.p. with the product obtained from compound III proved the structure of VII (total yield calc. as disodium salt 505 mg, 72 %).

*4) from the phenolic β-guaiacylether I.* A solution of compound I (300 mg) in white liquor (10 ml) was heated in an atmosphere of nitrogen on a water bath (100°). A colourless substance precipitated very slowly. After 4 days of heating the precipitate was filtered off and treated as described for the product obtained from compound V (see above), yield: 61 mg, 32.5 %. M.p. 249.5–250.5° and mixed m.p. proved it to be the dithiane VII. The filtrate was heated under the same conditions for another 6 days, whereupon an additional 71 mg were precipitated.

*Formation of dithiane XVII.* The *p*-hydroxy-benzylthioacetate XV (690 mg), when treated with 2 N sodium hydroxide at 100° in an atmosphere of nitrogen for 24 h, afforded a white precipitate which was centrifuged off, repeatedly washed with ethanol and dried *in vacuo*. Yield 335 mg, 87.5 %.

From a part of this sodium salt (40 mg) the free dithiane XVII was prepared by dissolving in water (2 ml), acidifying with 2 N hydrochloric acid, centrifuging off the white precipitate formed, washing with water and drying (21 mg, 57.5 %). Recrystallisation from ethanol yielded slightly impure *2,5-di-(4-hydroxy-3-methoxy-phenyl)-3,6-di-*

*hydroxymethyl-1,4-dithiane* (XVII) as small prisms. (Found: C 55.94; H 5.92; O 22.81; S 15.52. $C_{20}H_{24}O_6S_2$ requires: C 56.58; H 5.70; O 22.61; S 15.11).

Another part of the sodium phenolate of XVII (30 mg) was dissolved in acetic anhydride (1 ml) and the solution was kept at room temperature over-night. From the reaction mixture *2,5-di-(4-acetoxy-3-methoxy-phenyl)-3,6-di-acetoxymethyl-1,4-dithiane* could be isolated in the usual way. Recrystallisation from chloroform-hexane gave prisms, m.p. 148.5–150.5°, yield 37 mg, 97 %. (Found: C 56.87; H 5.60; O 26.97; S 10.50. $C_{28}H_{32}O_{10}S_2$ requires: C 56.74; H 5.44; O 27.00; S 10.82).

*Treatment of dithiane VII with white liquor at 170°.* Compound VII (100 mg, S = 17.6 %) was heated with white liquor (3 ml) in a stainless steel autoclave at 170° for 2 h in an atmosphere of nitrogen. Neutralisation of the solution with carbon dioxide yielded an amorphous precipitate (40 mg, S = 5.3 %) which was investigated by thin-layer chromatography. The chromatographic pattern showed great similarities with that given by the crude mixture of substances obtained from compound I after the same treatment with white liquor. The latter mixture contained 7.19 % sulphur.

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