

Cleavage of β -Aryl Ether Bonds in Phenolic Lignin Model Compounds with Anthrahydroquinone and Anthrone

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The equal abilities of anthrone and anthrahydroquinone to cleave β -0–4 bonds in phenolic structural units in lignin have been demonstrated with the aid of two model compounds. The structure of a degradation product, *trans*-isoeugenol, indicates that the cleavage involves an adduct having *erythro* configuration.

The “catalytic” effect of anthraquinone on delignification in alkaline pulping processes is believed¹ to derive, at least in part, from the ability of reduced forms of anthraquinone to cleave the aryl ether bond in phenolic β -0–4 structural units in lignin (for nomenclature, see Ref. 2).

In a previous article³ we have described the reaction of lignin model compound 1 with anthrahydroquinone in alkaline solution. The aryl ether bond was cleaved cleanly in a reaction that resembles the action of hydrosulfide ion on similar structures in kraft cooking.³

The terminal group in the side chain of 1 is methyl. In lignin this is usually a primary alcohol group and for structures like 2 the dominant reaction in alkaline solution is a retro-aldol reaction in which an enol ether is formed without cleavage of the aryl ether bond.⁴ To find out whether the reaction with anthrahydroquinone is able to compete with the retro-aldol reaction, we heated model compound 2 with an alkaline solution of anthrahydroquinone under similar conditions as compound 1.

Recent work⁵ has shown that some of the anthrahydroquinone in pulping reactions is reduced to the oxidation level of anthrone and that this may lead to irreversible reactions with quinone methides in lignin.^{6a} We have now found that anthrone cleaves the aryl ether bond both in 1 and 2 at rates comparable to those of anthrahydroquinone under

similar conditions.

The exclusive formation of the *trans* isomer or isoeugenol from 1 indicates that some stage in the reaction occurs with a high degree of stereospecificity.

RESULTS AND DISCUSSION

Experiments with anthrahydroquinone. The yields of liberated guaiacol (2-methoxyphenol) as a function of reaction time at 140 °C are shown in Fig. 1. As can be seen, the aryl ether bond is cleaved at similar rates in 1 and 2 under the chosen conditions, and the difference between the cleavage rates with and without the additive is larger for 2 than for 1. The conclusion can be drawn that the retro-aldol

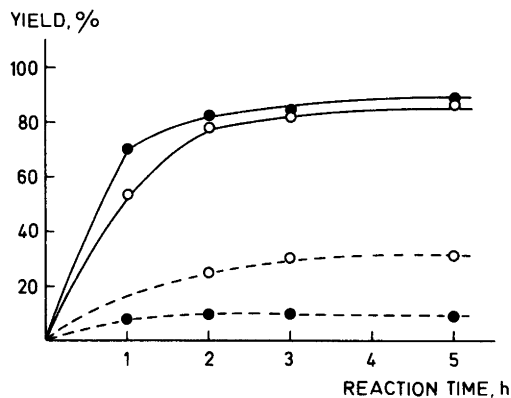
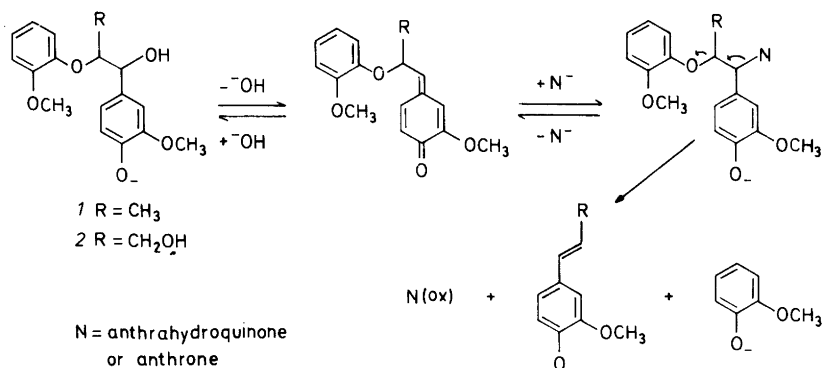


Fig. 1. Formation of guaiacol on treatment of 1 (○) (8.2×10^{-3} mol/l, from Ref. 3) and of 2 (●) (8.2×10^{-3} mol/l) in 1 M sodium hydroxide (40% dioxane) with anthrahydroquinone (—) and without anthrahydroquinone (---) at 140 °C.



Scheme 1. Phenolic compounds are depicted as anions.

reaction does not compete with the aryl ether cleavage in this case (*cf.* also Ref. 7).

Experiments with anthrone. When compound 2 was heated with an alkaline solution of anthrone at 140 °C for 3 h, the amount of guaiacol released was almost as large as with anthrahydroquinone (Table 1). This demonstrates that anthrone is as effective as anthrahydroquinone in cleaving phenolic β -O-4 ethers. A similar effect can be seen with compound 1 after heating it for 2 and 3 h with anthrone (Table 1). The yield of isoeugenol [2-methoxy-4-(1-propenyl)-phenol] from 1 is significantly lower in the reaction with anthrone, indicating that anthrone reacts irreversibly with some of the isoeugenol or with the quinone methide intermediate (Scheme 1). An adduct between anthrone and a quinone methide intermediate has been prepared^{6b} and shown to be

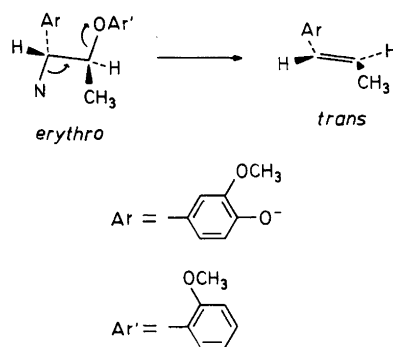
more resistant to alkaline degradation than the corresponding anthrahydroquinone adducts, although "extensive" degradation is reported at higher temperatures.^{6b} The mechanisms of these reactions are under investigation.

The stereochemistry of the aryl ether cleavage reaction. The isoeugenol formed in the aryl ether cleavage reaction of compound 1 is invariably the *trans* isomer (>99%). Since we have not been able to detect any *cis-trans* isomerization of isoeugenol under the present cooking conditions, we conclude that the exclusive formation of the *trans* isomer is a consequence of the stereochemistry of the cleavage reaction. If the cleavage is viewed as a heterolytic fragmentation,⁸ as has been suggested,⁹ the "electrofugal" and the "nucleofugal" groups will be antiperiplanar in the transition state. Such a transition state will lead to *trans*-isoeugenol only if the intermediate adduct has the *erythro* structure shown in Scheme 2.

Table 1. Yields of guaiacol and *trans*-isoeugenol on treatment of 1 (8.2×10^{-3} mol/l) and 2 (8.2×10^{-3} mol/l) in 1 M sodium hydroxide (40% dioxane) with an excess of anthrahydroquinone (AHQ) or anthrone (AN) at 140 °C.

Model compound	Reagent	Reaction time/h	Yield/%	
			Guaiacol	<i>trans</i> -Isoeugenol
1	AHQ	3	80.6 ^a	67.1 ^a
		2	78.5 ^a	72.5 ^a
	AN	3	84.6	50.3
		2	69.6	56.2
2	AHQ	3	85.1	
	AN	3	80.8	

^aRef. 3.



Scheme 2. Phenolic compounds are depicted as anions.

EXPERIMENTAL

1-(4-Hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-1-propanol (1).¹⁰ The yield of the *erythro* isomer was improved by lowering the temperature of the borohydride reduction step to 6 °C.¹¹ 1-(4-Hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol (2)¹² was obtained as a 1:1 mixture of *erythro* and *threo* isomers (m.p. 78–85 °C). Anthrahydroquinone diacetate was prepared from anthraquinone.¹³ The *isoeugenol* (FLUKA, *purum*) was a mixture of *cis* and *trans* isomers (20.5% *cis* according to GLC analysis) and was used as such for the isomerization experiment. Pure *trans* isomer was obtained by recrystallization of the acetylated material and hydrolysis of the *trans* acetate.¹⁴

The anthrahydroquinone and anthrone cookings. Anthrahydroquinone (AHQ) was generated from the stable diacetate in the reaction mixture. The cookings were run with model compounds 1 (ca. 90% *erythro*) or 2 (ca. 50% *erythro*) (0.082 mmol) dissolved in peroxide-free dioxane (4.0 ml), an excess of anthrahydroquinone diacetate or anthrone (Koch-Light) (375.0 mg), 2 M sodium hydroxide (5.0 ml) and water (1.0 ml) in Pyrex glass ampoules. Before being sealed, the ampoules were evacuated and flushed twice with oxygen-free nitrogen. In anthrahydroquinone experiments the ampoules were heated in an oil bath at 140 °C for 1, 2, 3, or 5 h. In anthrone (AN) experiments heating was at 140 °C for 3 h in the case of 2 and for 2 or 3 h in the case of 1. A warm-up time of two minutes was not included in time at temperature.

Cooling was for 5 min at room temperature and then in cold water. Ampoules were opened and the contents immediately neutralized with dilute acetic acid. The precipitate was filtered off and washed with chloroform (2 × 2 ml) and the filtrate was extracted with chloroform (5 × 2 ml). The combined chloroform layers were dried with sodium sulfate, which was filtered off and washed with chloroform (2 × 1 ml). After addition of the internal standard (methyl anisate), the combined solutions were chromatographed without derivatization of the components.

Cookings without any additives were carried out as above but in 0.75 M instead of 1 M sodium hydroxide solutions.

Recovery tests were run in a nitrogen atmosphere with guaiacol (5.9–6.3 mg) and *trans*-isoeugenol (5.7–6.8 mg) dissolved in peroxide-free dioxane (4.0 ml), anthrahydroquinone diacetate or anthrone (375.0 mg), 2 M sodium hydroxide (5.0 ml) and water (1.0 ml). The ampoules were heated at 140 °C for 1.5 h. The alkaline contents were worked up as above. The losses of guaiacol (14.0% with AHQ and 14.1% with AN) and isoeugenol (8.1% with AHQ and 15.8% with AN) in the cooking and extraction

processes were taken into account when calculating the results.

The isomerization experiments were run with the commercial mixture of *cis* and *trans* isoeugenol (11.1 mg) dissolved in peroxide-free dioxane (4.0 ml), anthrahydroquinone diacetate (375.0 mg), 2 M sodium hydroxide (5.0 ml) and water (1.0 ml) in glass ampoules. Isomerization experiments without anthrahydroquinone were carried out in 0.75 M sodium hydroxide solutions. The ampoules were heated at 140 °C for 3 h. After working up the reaction mixtures as described above, GLC analysis revealed no significant isomerization. The percentage of *cis* isomer was 20.3% without AHQ and 16.9% with AHQ.

Gas chromatography was performed as described previously.³

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