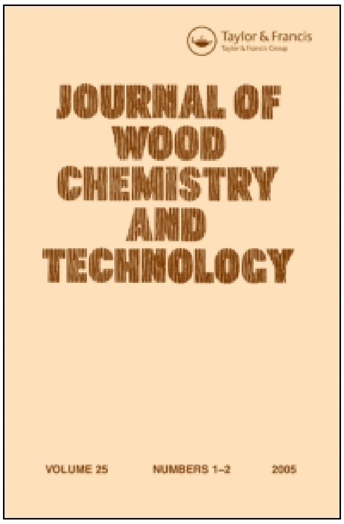

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ARYL MIGRATIONS DURING PULPING *

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Dedicated to the memory of Kyosti V. Sarkanen

ABSTRACT

Aryl migrations taking place during pulping processes are described. Migrations from C_α to C_β are given by "condensed" β-O-4 units and result in fragmentation and the formation of potential chromophoric systems of the stilbene type. Migrations from C_β to C_α, on the other hand, are observed with stilbenoid units and their precursors (β-1 and β-5 units) and afford 1,1-diaryl-2-oxo structures. Both types of aryl migration proceed via 3-membered spiro-cyclohexadienone intermediates. The direction of the aryl migrations may affect the ease and extent of lignin fragmentation and the formation of potential chromophoric groups during pulping processes.

INTRODUCTION

It is well known that condensation reactions hamper lignin degradation and lignin dissolution during pulping processes. The course of these condensation reactions in alkaline media involving only phenolic lignin units has been formulated[1] as is schematically outlined in Figure 1.

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* This review was presented at the 6th International Symposium on Wood and Pulping Chemistry, Melbourne, April 19-May 3, 1991, Proceedings, Vol. 1, pp. 251-253

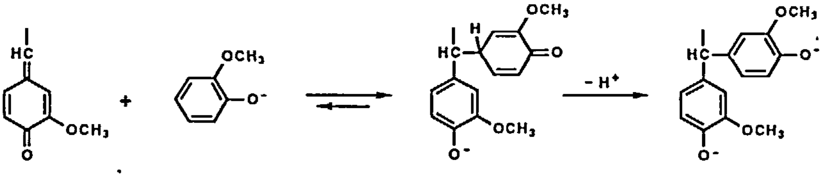


Figure 1 Condensation of phenolic lignin units in alkaline media.

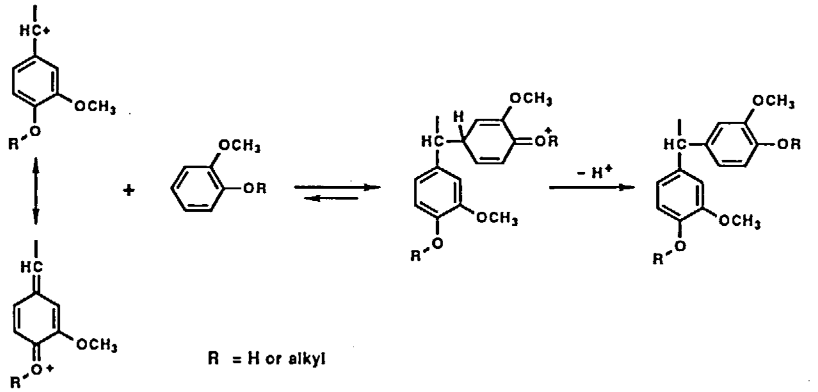


Figure 2 Condensation of phenolic and non-phenolic lignin units in acidic media.

One phenolic unit attacks nucleophilically the electron-deficient α-carbon atom of an intermediate quinone methide structure in another lignin unit (Michael addition) giving rise to a cyclohexadienone structure which loses a proton, affording a condensation product of the 1,1-diarylpropane type. The driving force in both steps is rearomatization, first of the quinone methide, and then of the cyclohexadienone intermediate.

In acidic media, analogous reactions are given by both phenolic and non-phenolic units[2]. Instead of quinone methide and cyclohexadienone intermediates, the corresponding conjugate acids, i.e. quinonium methide and cyclohexadienonium ions are formed, as shown in Figure 2.

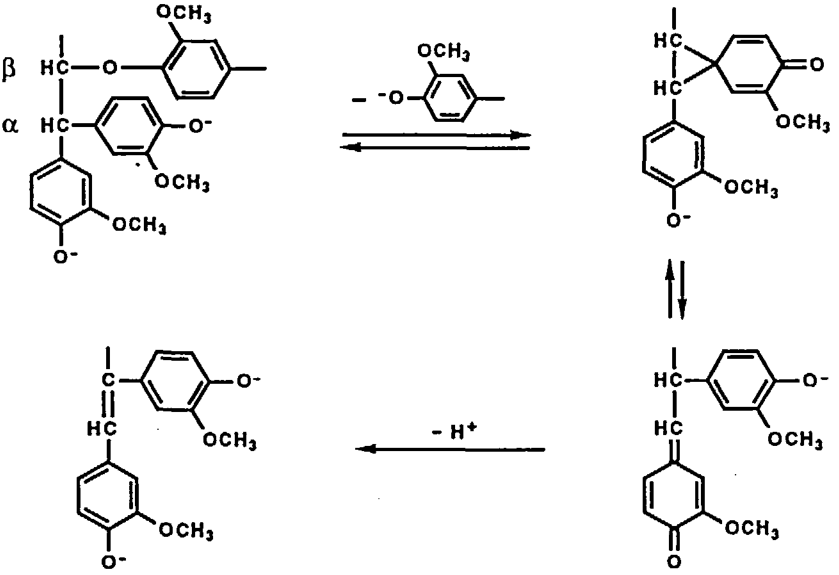


Figure 3 Migration of aryl residues from C_α to C_β in alkaline media. Formation of stilbenes.

Lignin condensation is thus due primarily to the introduction of the aryl residue of a lignin unit into the α-position of the side chain in another lignin unit which results in the formation of a covalent C-C bond between the lignin molecules involved.

However, if the condensation has taken place in a β-O-4 structure, as shown in Figure 3, one of the α-aryl residues can migrate to the β-carbon atom and displace the aroxy substituent[3]. In this way, a separation of two adjacent lignin units is achieved, which means that *lignin condensation* is followed by the opposite process, i.e. by *lignin fragmentation*.

ARYL MIGRATIONS FROM C_α to C_β

Alkaline Media

Figure 3 describes the course of an aryl migration from C_α to C_β, taking place in phenolic condensed lignin units of the β-aryl ether (β-O-4) type during alkaline

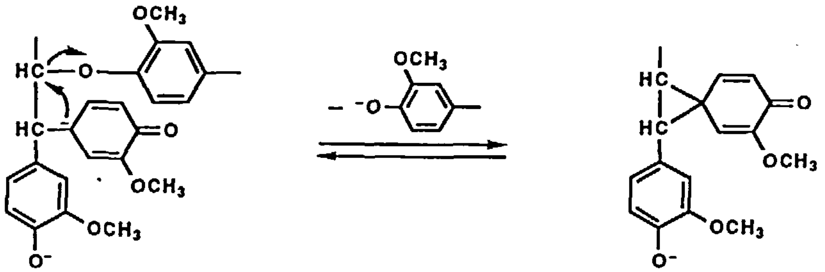


Figure 4 The rate-determining step of C_α to C_β aryl migration.

cooking. This type of reaction has been extensively studied[4] and interpreted in terms of a nucleophilic attack on the electron-deficient β-carbon atom by one of the phenolate anions (in the carbanion form), followed by opening of the 3-membered ring in the spiro-cyclohexadienone intermediate. The latter step is assisted by the phenolate moiety. Proton elimination with re-aromatization and the formation of a stilbenoid structure terminates the course of events. This conversion of a condensed β-O-4 structure into a stilbenoid structure parallels a well established precedent, i.e., the alkaline solvolysis of 2-p-hydroxyphenylethyl bromide[5,6].

Thus, the reaction is reminiscent of the preceding condensation reaction:
Both types of reaction start with a nucleophilic attack on an electron-deficient centre. In the condensation reactions, this centre is the methylene carbon atom in a quinone methide intermediate (Figure 1). In the aryl migration reactions, the electron-deficient centre is the β-carbon atom in the condensed unit (Figure 3).
In both types of reaction, the nucleophilic attack is followed by proton elimination, resulting in re-aromatization.

Kinetic studies of this aryl participation (A_1-3) reaction using C-1 deuterium labelled substrates showed that the intramolecular nucleophilic displacement of the aryloxy moiety by the cyclohexadienone carbanion, outlined in Figure 4, is the rate-determining step and that the reaction rate is enhanced by electron-donating substituents on the migrating aromatic ring[4]. The migratory aptitude of aromatic rings was found to be dependent on the nature and location of these substituents. Figure 5 shows the Hammett-Brown correlation of the effects of methyl and methoxyl substituents on the migratory aptitude of phenolic nuclei.

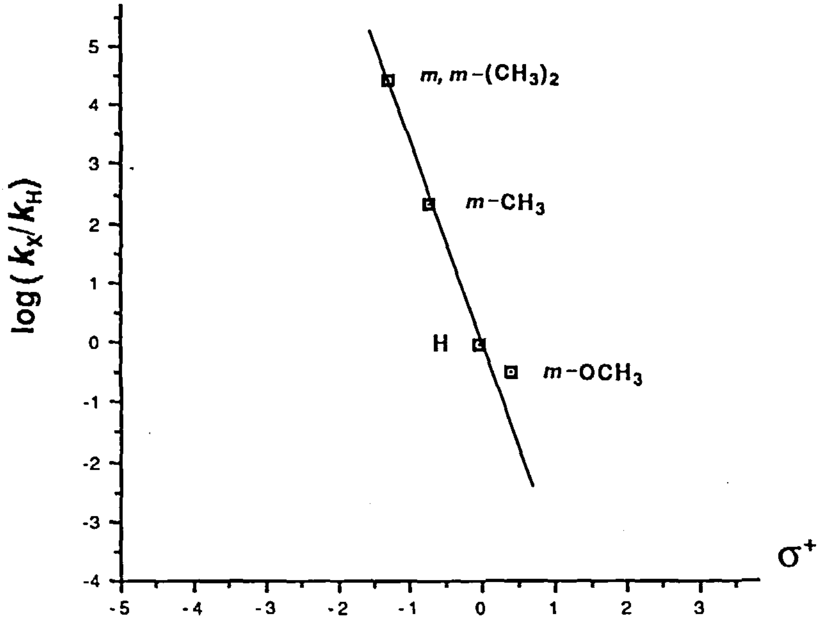


Figure 5 Hammett-Brown correlation of substituent effects on the migratory aptitude of phenolic nuclei.

These effects of the substituents on the reaction rate are consistent with the supposition that the migrating group participates in the transition state of the rate-determining step (Figure 4) of the overall reaction.

Comprehensive model studies revealed that these C_α to C_β migrations in alkaline media are limited to phenolic structures and require two phenolic nuclei attached to the α-carbon atom[3,4].

Experimental support for the validity of the proposed mechanism was also provided by treating wood shavings with 2,6-xylenol in alkaline solution at elevated temperature and isolating the expected 4,4′-dihydroxy-3-methoxy-3′,5′-dimethylstilbene from the reaction mixture[7].

Condensed β-aryl ether structures containing the phenolic hydroxyl group in the ortho-position relative to the condensation site give an analogous aryl migration and conversion into the corresponding stilbene (Figure 6, right-hand side).

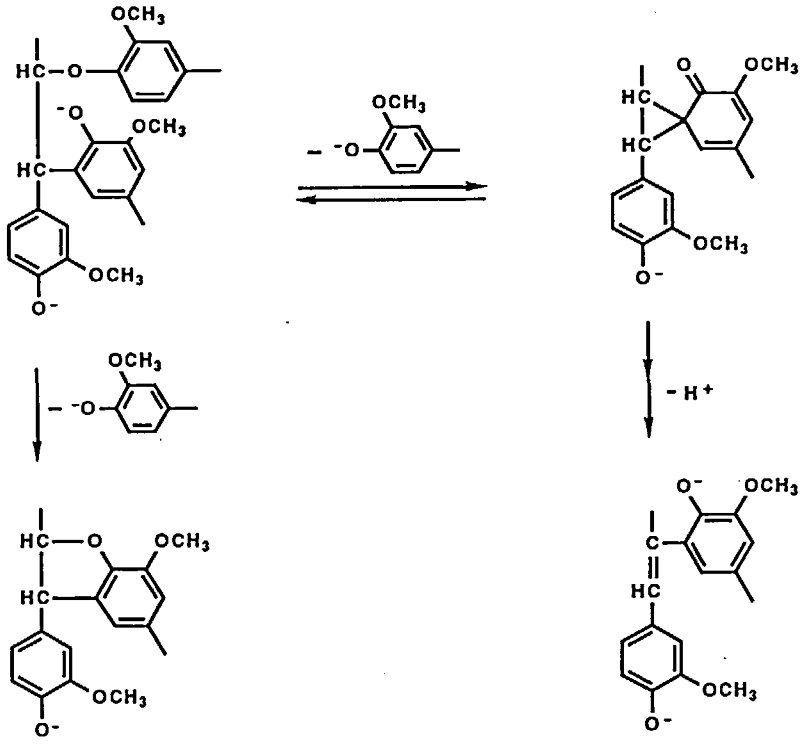


Figure 6 Migration of aryl residues from C_α to C_β in alkaline media. Formation of stilbenes in competition with the formation of 3-arylcoumarans.

However, such structures also undergo another type of neighbouring group participation, yielding 3-arylcoumarans[2,3,7], as shown in the left-hand part of the Figure. In this competing reaction, the ortho-phenolate anion attacks nucleophilically the β-carbon atom and eliminates the β-aroxy substituent. Thus, both neighbouring group participation reactions result in the cleavage of the β-aryl ether bond, i.e., in lignin fragmentation.

The mechanism of C_α to C_β aryl migrations strongly resembles that of another heterolytic fragmentation process, i.e., the sulfidolytic cleavage of β-aryl ether linkages[8]. Figures7 and 8 illustrate the similarities between these two processes.

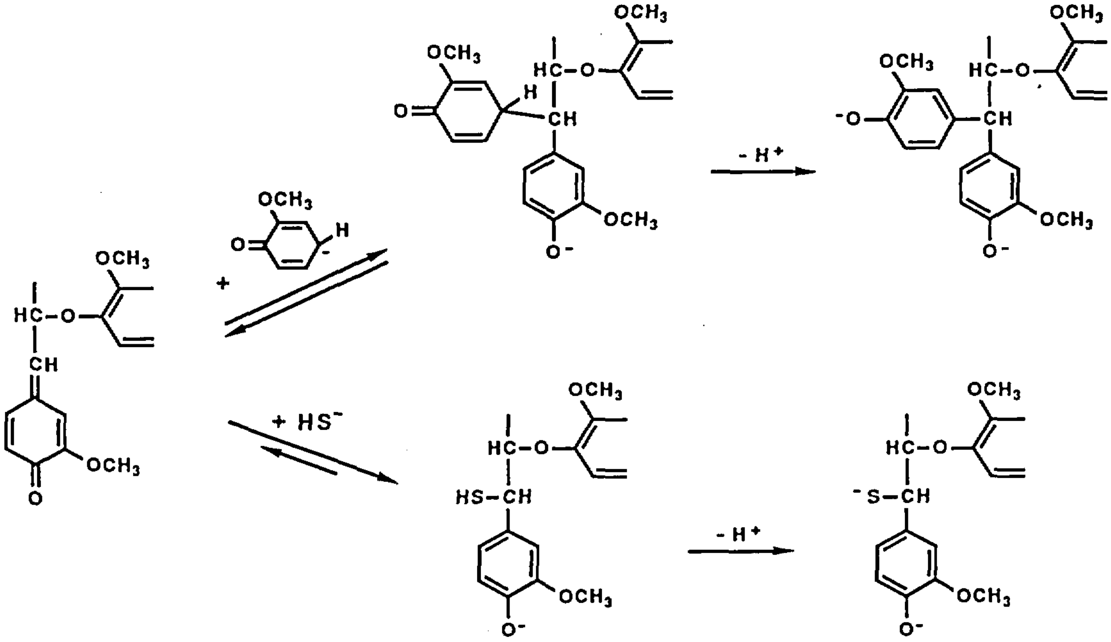


Figure 7 Parallels between sulfidolytic β-aryl ether cleavage and β-aryl ether cleavage by aryl migration. Incorporation of the splitting species.

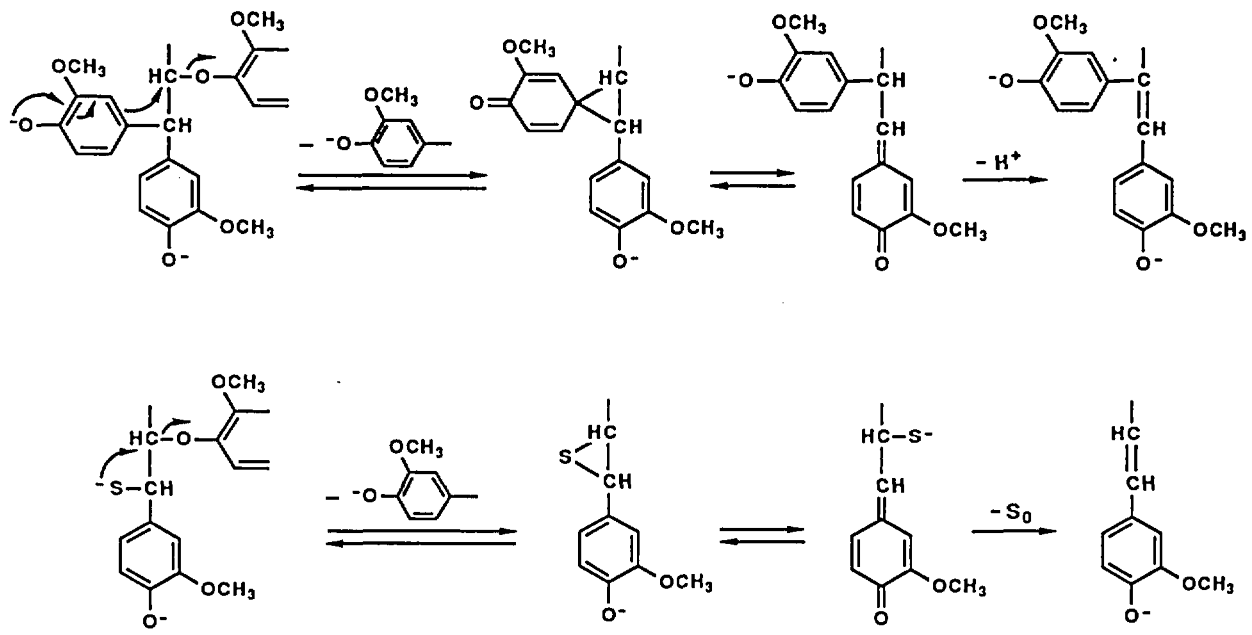


Figure 8 Parallels between sulfidolytic β-aryl ether cleavage and β-aryl ether cleavage by aryl migration. Neighbouring group participation. Formation of ring-conjugated structures *via* 3-membered intermediates.

The first step, the incorporation of the splitting reagent, is analogous: addition of a phenolate anion (in the carbanion form) or a hydrosulfide anion to quinone methide intermediates is followed by proton elimination with the formation of an α-phenolate or an α-mercaptide anion.

The similarities between the two subsequent neighbouring group participation reactions, resulting in migration of the splitting reagents from C_α to C_β with concomitant elimination of the aroxide anion, are also striking, as shown in Figure 8: In both cases, the migration involves intramolecular nucleophilic attack on the neighbouring β–carbon atom and proceeds via 3-membered ring intermediates of the spiro-cyclohexadienone- or thiirane type. These then undergo aroxide anion-assisted opening of the 3-membered ring and elimination of a proton or of elemental sulfur with the formation of the corresponding hydroxy-substituted styrenes or stilbenes.

In comparative studies of the efficiency of various participating neighbouring groups with respect to the cleavage of β–aryl ether bonds, it was found[9] that α-mercaptide groups, because of their stronger nucleophilicity, are far superior to α-phenolate groups.

Acidic Media

Aryl migrations from C_α to C_β in condensed units of the β–O-4 type are also observed in acidic media (Figure 9). Protonation of the β–aryl ether oxygen facilitates the separation of the aroxy group as a phenolic residue from the parent structure which turns into a positively charged intermediate of the spiro-cyclohexadienonium type.

The reaction can be formulated analogously to that in alkaline media, a spiro-cyclohexadienonium ion instead of a spiro-cyclohexadienone arising as intermediate.

The occurrence of such migrations is indicated by the products formed when model compounds of the β-aryl ether type are treated with an excess of simple phenols in strongly acidic media. In the reaction mixtures, condensation products of the α,β-diaryl type, shown in the right-hand part of the figure, were found together with small amounts of the expected stilbene, shown in the left-hand part of the Figure[10].

The formation of the stilbene can be explained in the usual way, i.e., by an aryl-assisted opening of the spiro-ring in the cyclohexadienonium intermediate,

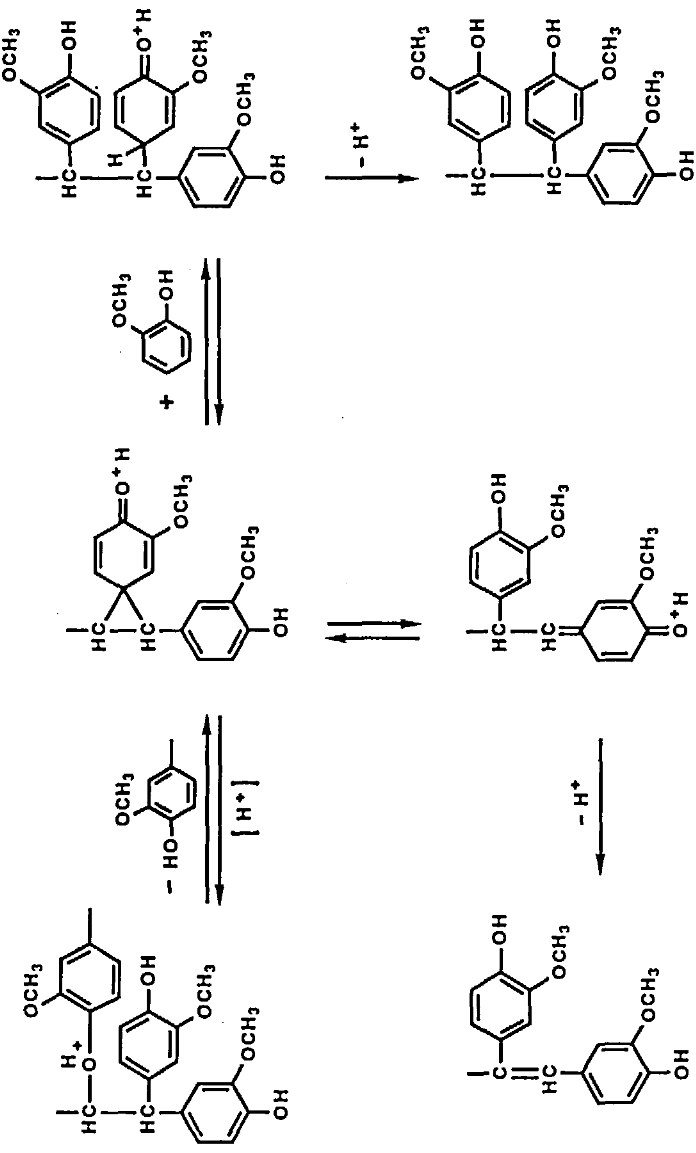


Figure 9 Migration of aryl residues from C_α to C_β in acidic media. Formation of condensation products of the 1,1,2-triarylpropane type.

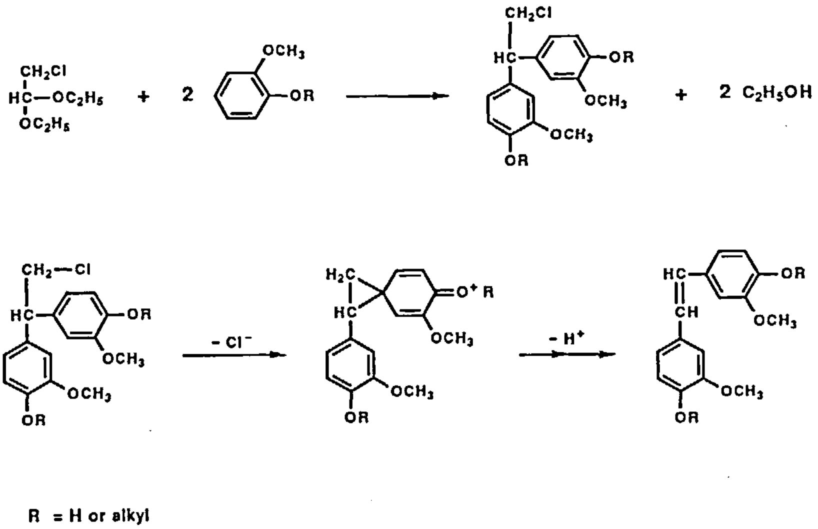


Figure 10 Course of stilbene synthesis. Acidic condensation, followed by aryl migration.

followed by proton elimination. The condensation products of the α,β-diaryl type should arise in a second condensation step through nucleophilic attack by a further phenol molecule on the spiro-cyclohexadienonium intermediate, also followed by proton elimination.

It seems likely that reactions of this type can take place under the conditions of acid-catalyzed organosolv pulping and during phenolysis of wood, i.e., during cooking of wood with phenols in acidic medium.

The feasibility of the reaction mechanism involving acidic condensation followed by acid-promoted aryl migration is also supported by the course of the stilbene synthesis[11], outlined in Figure 10.

After treatment of monochloroacetaldehyde diethylacetal with appropriate phenols or phenol ethers in acidic medium at elevated temperature, the corresponding stilbene (or stilbenes) can be obtained. There is no need to isolate the intermediary condensation product. In the case of phenolic compounds, i.e., if R equals H, the second step (aryl migration) can also be achieved in alkaline media.

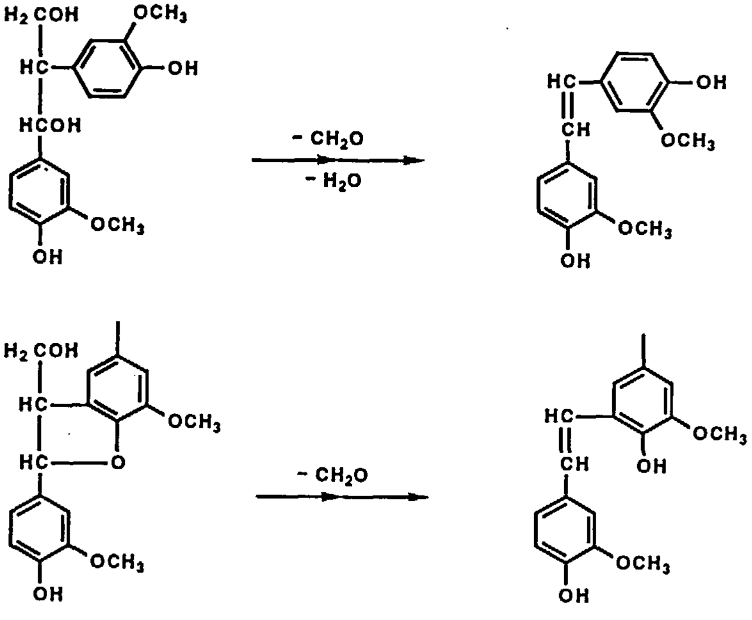


Figure 11 Formation of stilbenoid structures from native structures of the 1,2-diarylpropane-1,3-diol- (β-1) and arylcoumaran (β-5) types.

Alkali- and acid-promoted aryl migrations from C_α to C_β involve cleavage of β-aryl ether bonds (fragmentation) and generate potential chromophores of the stilbene type, in addition to those formed during pulping[1] from the native structures of the 1,2-diarylpropane-1,3-diol (β-1) and arylcoumaran (β-5) types (Figure 11).

ARYL MIGRATIONS FROM C_β to C_α

Aryl migrations from C_β to C_α are encountered under various *acidic* conditions, e.g. during acidolysis of model compounds of the 1,2-diaryl -1,3-diolpropane (β-1) type[12] (Figure 12).

The reaction sequence comprises protonation of the oxygen in hydroxyl, alkoxyl (R_1=alkyl) and aroxyl (R_1=aryl) groups and elimination of water, alcohol and/or phenol, followed by aryl migrations (pathways A and B) to give 1,1-diaryl-2-oxo derivatives.

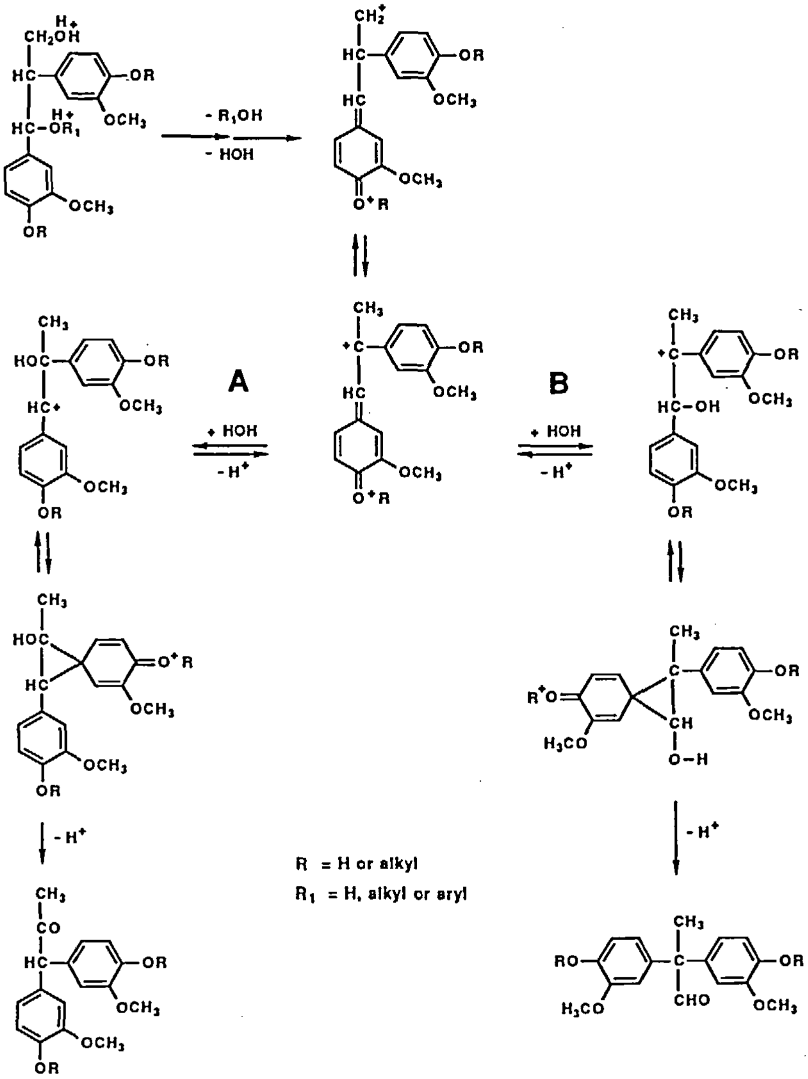


Figure 12 Migration of aryl residues from C_β to C_α during acidolysis.

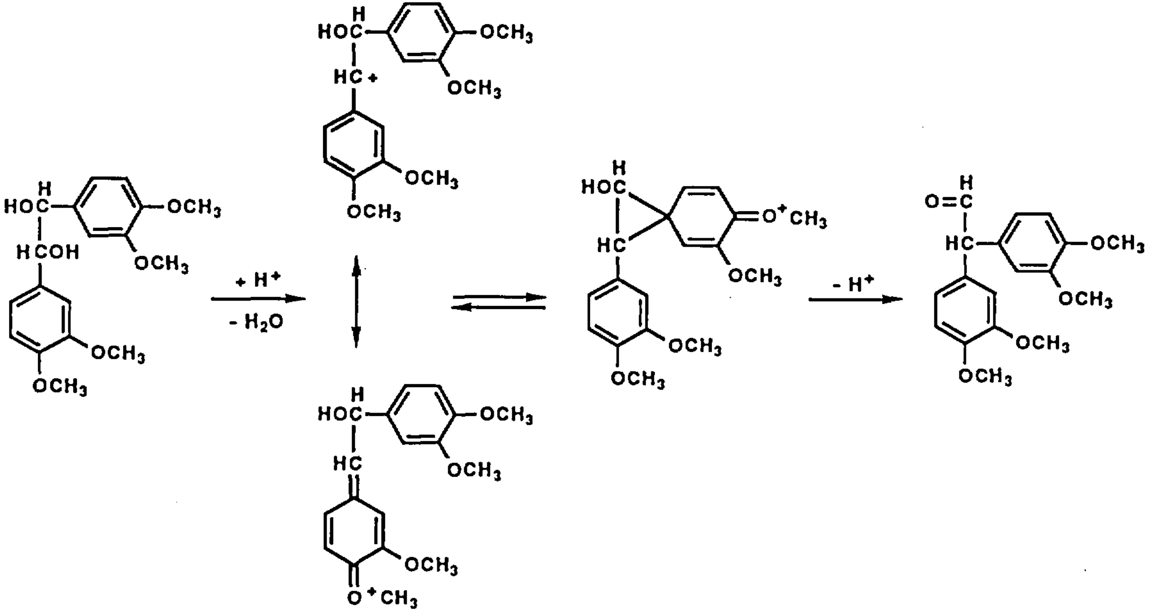
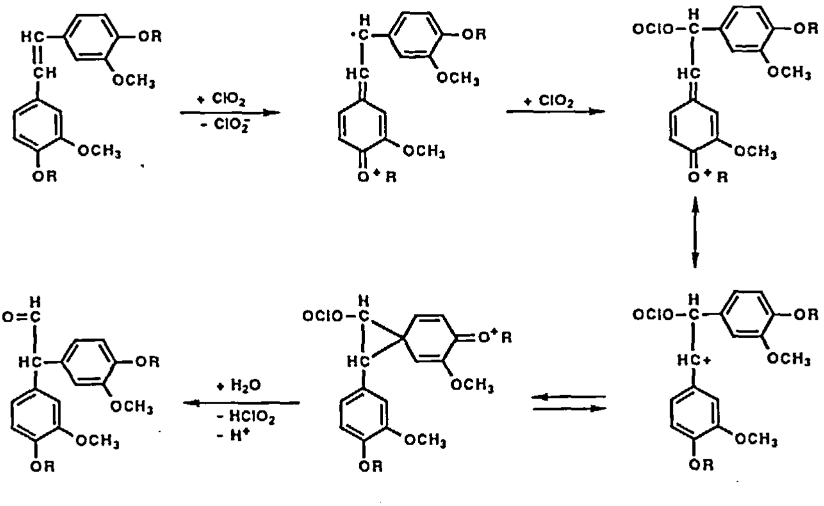


Figure 13 Acid-promoted C_β to C_α migration in a hydrobenzoin.



R = H or alkyl

Figure 14 C$_\beta$ to C$_\alpha$ migration in stilbenes during chlorine dioxide bleaching.

An aryl migration of this type is also observed in the acid-promoted rearrangement of hydrobenzoins[13] and related structures. The reaction, exemplified with the symmetrical tetramethoxy derivative (Figure 13, R=CH$_3$) results in the formation of the corresponding 1,1-diarylacetaldehyde.

In addition to these C$_\beta$ to C$_\alpha$ migrations which comprise only heterolytic steps, there are some important examples of C$_\beta$ to C$_\alpha$ migrations which are initiated by homolytic processes. Thus, when the same tetramethoxystilbene was treated with chlorine dioxide under bleaching conditions, the same diarylacetaldehyde as shown in Figure 13 was found in the reaction mixture among many other products[14]. The course of events may be outlined as shown in Figure 14.

In the first step, chlorine dioxide reacts with the stilbene to give the corresponding radical cation which is the common intermediate for all identified products obtained from this stilbene[14]. The radical cation then combines with a molecule of the bleaching reagent and the resulting chlorite ester of the methylene quinonium <--> benzylium ion type undergoes intramolecular electrophilic attack on the

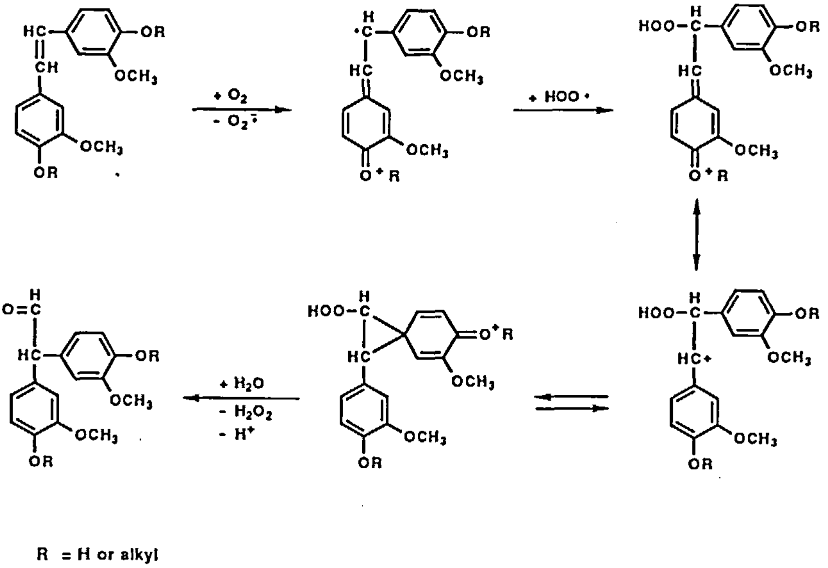


Figure 15 C_β to C_α migration in stilbenes during oxygen bleaching in acidic media.

aromatic ring by the electron-deficient carbon atom (benzylium ion) to give a spiro-cyclohexadienonium intermediate. Hydrolysis of the chlorite ester with concomitant rearrangement affords the 1,1-diarylacetaldehyde of Figure 13.

An analogous pathway is followed when the same starting compound, the tetramethoxystilbene, is treated with oxygen under acidic conditions at elevated temperature[15]. In this case, it is suggested that a hydroperoxy radical, instead of chlorine dioxide, adds to the radical cation intermediate.

Generally, the C_β to C_α migrations may be regarded as phenonium rearrangements (Wagner Meerwein rearrangements) in which the migrating aryl group undergoes intramolecular electrophilic substitution by the initially formed electron-deficient centre, i.e., the carbonium <--> phenoxonium ion.

CONCLUSION

Both types of aryl migration involve intramolecular attack. In the case of C_α to C_β migrations, it is a *nucleophilic* attack by carbanions on the electron-deficient β–carbon atom in β–aryl ether structures, whereas in the case of C_β to C_α migrations, it is an *electrophilic* attack by carbonium <--> phenoxonium ions on electron-rich centres in aromatric nuclei.

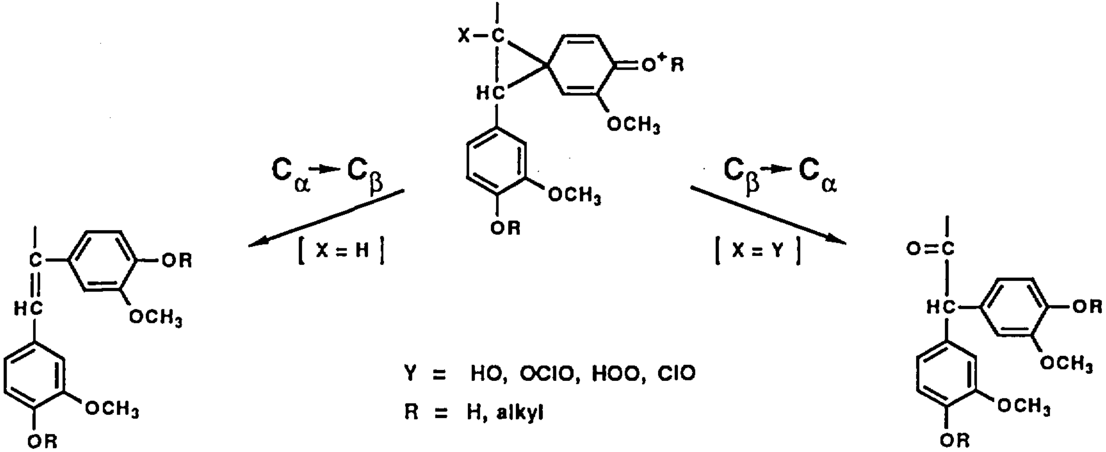
Both types of aryl migration proceed via 3-membered cyclic transients or intermediates. In an alkaline medium, spiro-cylohexadienones, and in an acidic medium spiro-cyclohexadienonium ions, are formed in reversible reactions.

These initial steps are followed by irreversible re-aromatization steps. The question as to what determines the direction of aryl migration, i.e., the site of opening of the spiro ring in the intermediates, may be tentatively answered as follows.

The common feature of C_α to C_β migrations is that the opening of the 3-membered spiro-ring is assisted by the transition of the aromatic ring, substituted by electron-donating hydroxyl or alkoxyl groups, into a quinone methide or quinonium methide moiety, as shown on the left-hand side of Figure 16 (X=H). In C_β to C_α migrations, however, the opening of the 3-membered spiro ring is promoted by an appropriate β–substituent (e.g. X equals Y) which determines the opposite direction of migration, as shown on the right-hand side of the Figure. In both cases, re-aromatization constitutes the driving force.

Aryl migrations from C_α to C_β, involving cleavage of β–aryl ether bonds, contribute to lignin fragmentation during cooking processes. These migrations are accompanied by the formation of potential chromophoric structures of the stilbene type. In subsequent oxidative bleaching steps, stilbenoid structures are more easily degraded than are the parent (condensed) β–aryl ether structures[15,16] and this degradation results in the separation of two neighbouring lignin units, i.e. in further lignin fragmentation. Thus, C_α to C_β migrations should have a beneficial effect on the degradation of lignin during both cooking and subsequent bleaching.

On the other hand, aryl migrations from C_β to C_α lead to the conversion of potential chromophoric systems of the stilbene type and of their precursors, i.e., 1,2-diarylpropane-1,3-diol (β-1) and arylcoumaran (β-5) structures, into



Y = HO, OClO, HOO, ClO

R = H, alkyl

Figure 16 The two directions of aryl migration.

1,1-diaryl-2-oxo structures. In subsequent bleaching steps, these carbonyl--containing structures may also be attacked by oxidants. However, unlike the oxidative cleavage of the olefinic double bond in stilbenes which results in separation of two adjacent moieties, the oxidation of the products of C_β to C_α migration, i.e., the 1,1-diaryl--2-oxo structures, affords carboxylic acids but does not lead to fragmentation. Thus, C_β to C_α migrations should not contribute to lignin degradation during cooking and should afford structures which are more resistant to oxidative fragmentation during subsequent bleaching.

This implies that the direction of aryl migration may be important for the ease and extent of delignification and also for the formation and/or elimination of potential chromophoric groups during pulping processes.

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