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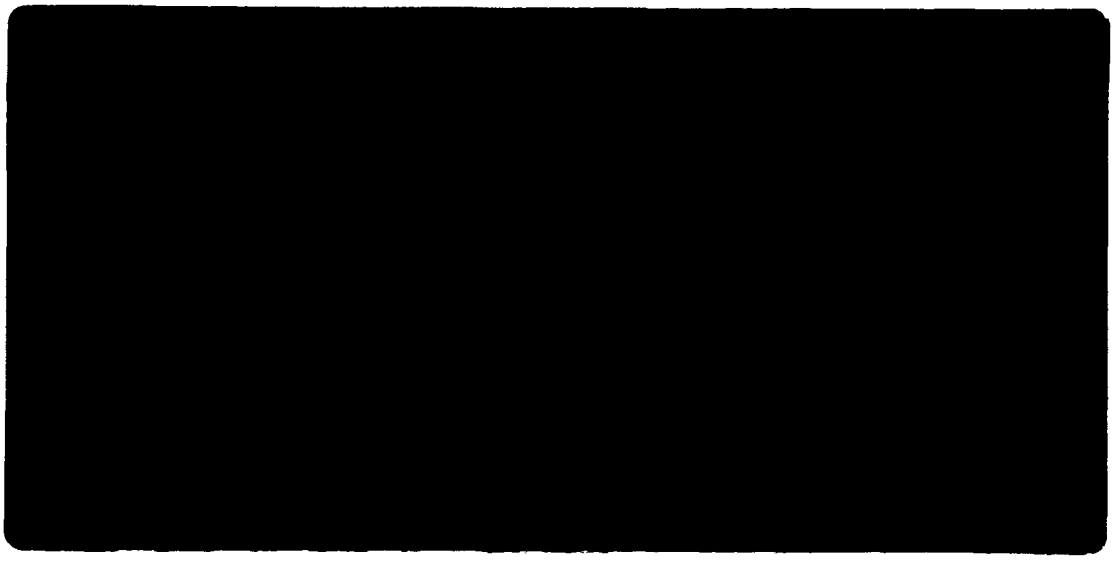

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INSOLUBLE LIGNIN MODELS (5): PREPARATION AND ALKALINE CONDENSATION REACTIONS OF A POLYMER-BOUND QUINONE METHIDE

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ABSTRACT

A lignin model, capable of forming a quinone methide in alkali, was bound to polystyrene and heated in alkali with 2,6-dimethoxyphenol. The polymer-supported phenol did not react with the soluble phenol under a variety of conditions, while an analogous non-bound phenol rapidly reacted with 2,6-dimethoxyphenolate ion, giving a condensation dimer in good yield. Condensation in the two-phased system appeared to be inhibited primarily by steric factors involving the supporting polystyrene resin.

INTRODUCTION

Lignin quinone methides (QMs) are important intermediates during alkaline pulping.[1] Pulping nucleophiles, such as the hydroxide, hydrosulfide, and anthrahydroquinone ion, react with QMs to fragment and subsequently dissolve the lignin macromolecule. Unfortunately, several undesirable reactions compete with the fragmentation reactions. Reaction of phenolic lignin nucleophiles with QMs can lead

to the generation of new carbon-carbon bonds between lignin moieties which are stable toward alkali.[2-4] Formation of these "condensed" materials impedes the complete removal of lignin during pulping.

We recently described the preparation[5] and condensation reactions[6] of a simple polymer-supported lignin model. The insoluble supported models provide a more realistic two-phased reaction interface not encountered in soluble model systems. Insolubility is an important aspect when studying pulping phenomena since most lignin reactions are believed to occur in the gel or solid phase.[7]

The relative rate for a soluble QM condensing with a polymer-supported, phenolic lignin model was significant, but slower by a factor of four than in the analogous soluble system.[6] In this paper, we discuss the preparation and alkaline condensation reactions of a polymer-bound QM with a soluble phenol (Scheme 1), which is essentially the reverse of our earlier study.

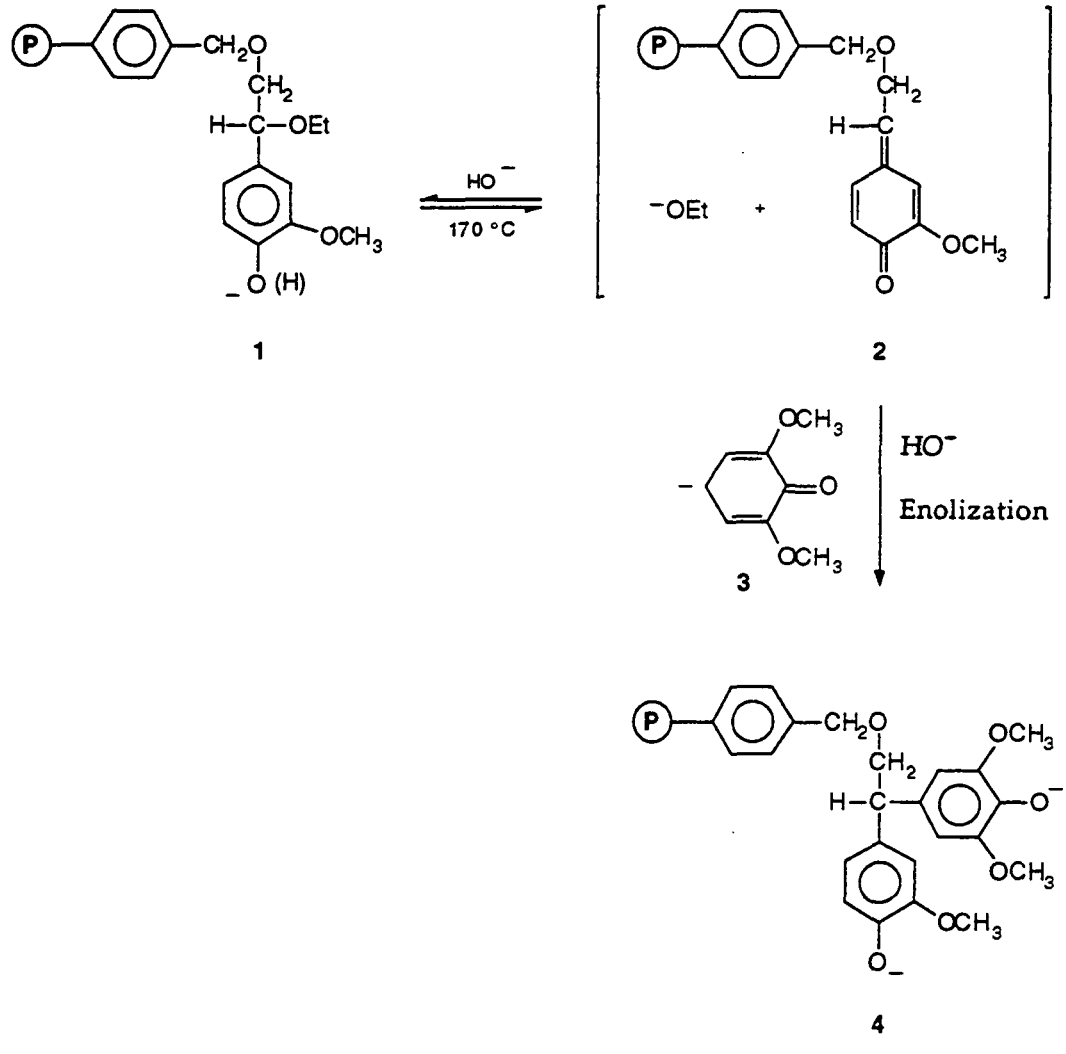
RESULTS AND DISCUSSIONS

Synthetic Approach

Polymer-supported QM model **1** was prepared (Scheme 2) according to the general approach taken in previous heterogeneous syntheses.[5,8] The first requirement involved the multistep preparation of a protected lignin model, 2-ethoxy-2-(3'-methoxy-4'-allyloxyphenyl)-1-ethanol (**6**). Both the phenolic and benzylic hydroxyl groups on **6** were protected as ethers, leaving the primary hydroxyl group on the β-carbon as the only site available for attachment to the heterogeneous support. Next, the primary alkoxide of **6** was condensed onto a modified polystyrene resin (**7**), resulting in heterogeneous intermediate **8**. The polymer-supported phenol (**1**) was finally produced by removal of the allyl protecting group. As shown in Scheme 1, the α-ethoxide on **1**

will be lost during the formation of QM **2** and therefore does not have to be removed to activate the supported model.

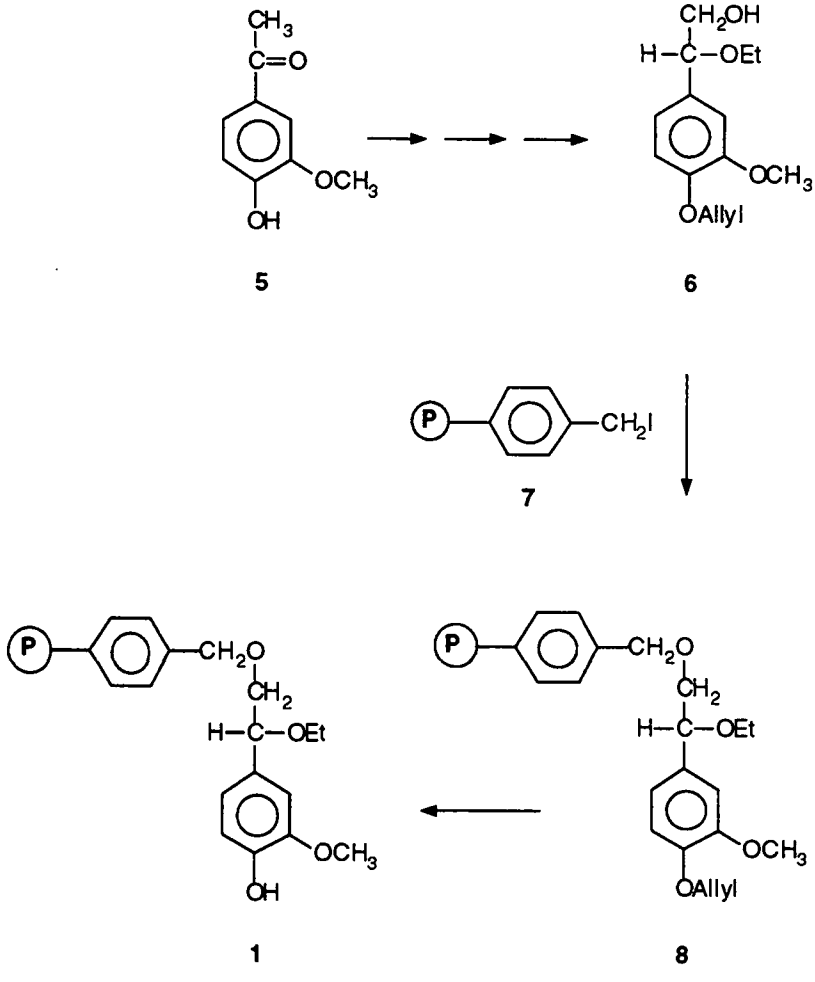
Scheme 1



The heterogeneous benzyl ether bond has demonstrated good stability under alkaline pulping conditions.[6] Aliphatic β-ether bonds, such as that in model **1**, are not susceptible to the usual neighboring group-type cleavage reactions experienced by the corresponding β-aryl ethers during pulping.[9] Characteristics of the supporting macro-

reticular polystyrene resin, Amberlite XE-305, have been described in earlier reports.5,8,10

Scheme 2



Preparation of the Quinone Methide Precursor (6)

The allyl protected α-ethoxy model (**6**) was prepared from acetovanillone **5** as illustrated in Fig. 1. Diacetate **10** was prepared from bromoketone **9**[11,12] according to a known method.[13] Deacetylation of **10** by hydrogen chloride in methanol has been successfully employed

by others;[13-15] however, we observed incomplete hydrolysis. Instead, sodium methoxide in methanol was employed to rapidly and effectively deacetylate **10**.

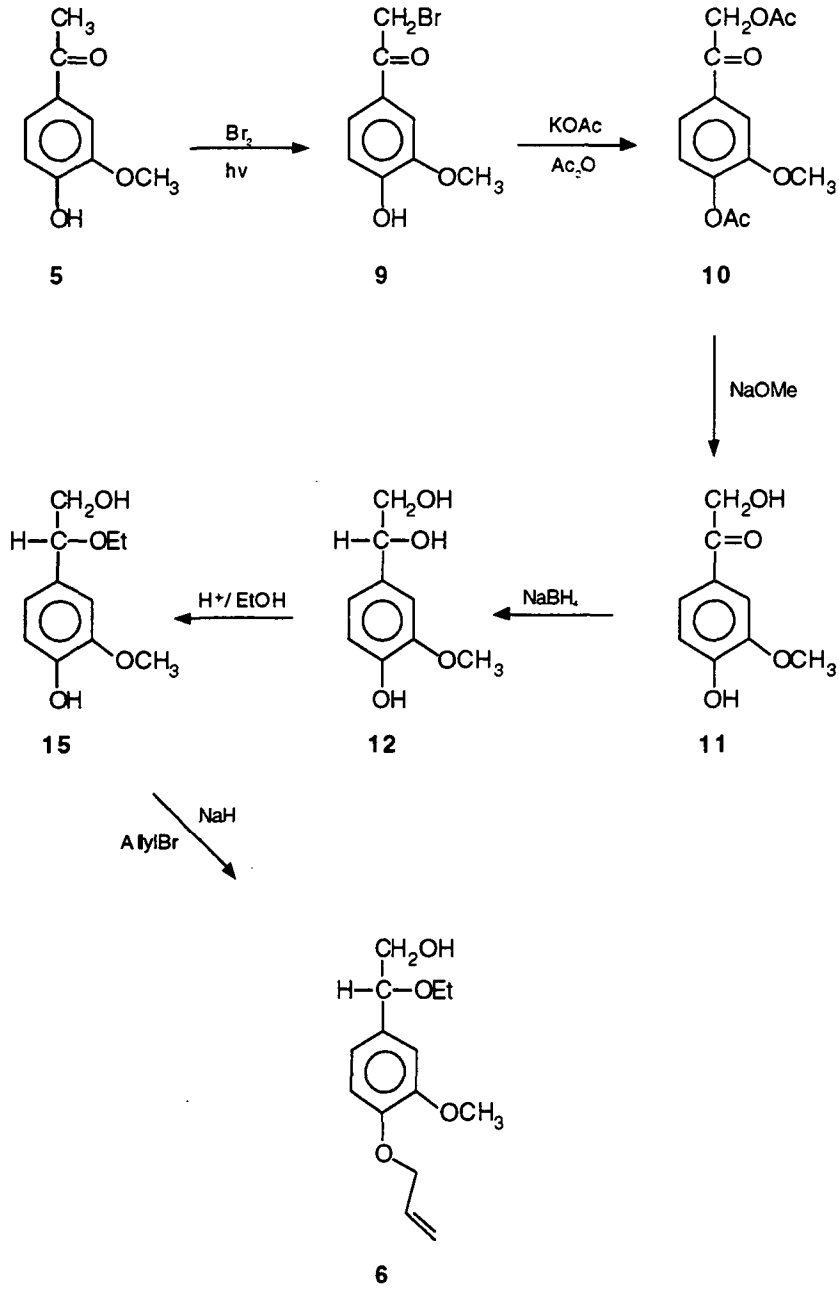
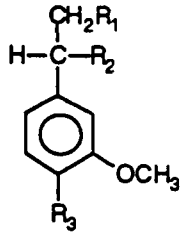
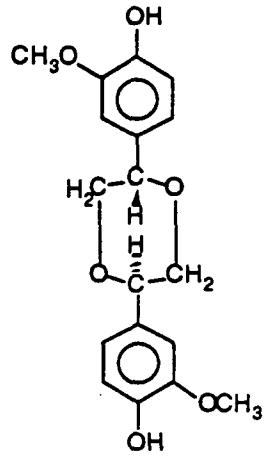


Figure 1. Preparation of model (**6**) which will be coupled to a polymer.

Reduction of **11** with sodium borohydride gave the glycol **12**, which was readily characterized as peracetate **13** and silyl derivative **14**. Holshouser and Kolb[16] reported that treatment of diacetate **10** with lithium aluminum hydride directly yielded the glycol **12** in moderate to low yield (46%). Several attempts at preparing the glycol with this procedure were unsuccessful.



13, $R_1=R_2=R_3=OAc$
14, $R_1=R_2=R_3=OSiMe_3$
16, $R_1=R_2=OEt$, $R_3=OH$
18, $R_1=R_3=OAc$, $R_2=OEt$



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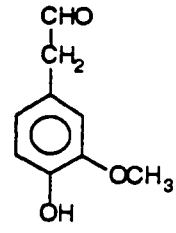


19

The glycol **12** was treated with anhydrous hydrogen chloride in ethanol to give a mixture composed mainly of ether **15**, along with small amounts of α,β-diethoxy product **16** and dimer **17**. A portion of pure α-ethoxide **15**, from crystallization of the crude product mixture, was acetylated; a ^{1}H-NMR spectrum of the resulting derivative **18** confirmed that the benzylic site had been selectively protected. The selectivity of methanolic hydrogen chloride for benzylic hydroxyl groups has been observed by others.[17-19]

Finally, the phenolic site of **15** was protected as an allyl ether to give **6**. The overall yield of allyl-protected model **6** was 18% based on bromoketone **9**.

Preparation of the Polymer-Supported Quinone Methide Precursor (1)

The approach (Scheme 2) to the preparation of heterogeneous model **1** resembled those discussed in earlier reports.[5,8] The allyl-protected model **6**, as its alkoxide, was condensed onto iodomethylated resin **7** to give polymer-supported model **8**. The resin **8** was characterized by its lower iodine content and by its fourier transform infrared (FTIR) spectrum (see Experimental Section). Next, most of the residual benzyl iodide units on **8** were converted to nonreactive methyl ethers by treatment with sodium methoxide in methanol. The iodine content fell from 9.3 to 1.9%; the FTIR spectrum showed few changes.

The final step in the preparation of phenolic, polymer-supported model **1** was removal of the allyl group by: (1) isomerization to a prop-1-enol ether group with tris(triphenylphosphine)rhodium(I) chloride (TTPPR) and 1,4-diazabicyclo[2.2.2]-octane (Dabco), and (2) hydrolysis of the resulting vinyl ether. While acid hydrolysis had proved effective with other allyl-protected phenols,[5] such was not the case with the current model which demonstrated a sensitivity to acidic conditions. To conserve polymer-bound material, we performed several test reactions on the soluble allyl-protected compound **6** to determine the general stability of the model to the conditions encountered during removal of the allyl group.

Treatment of **6** with TTPPR/Dabco in a refluxing mixture of ethanol/benzene/water gave the corresponding prop-1-enol ether as desired. However, subsequent reaction of the intermediate ether with dilute hydrochloric acid in acetone resulted in a product mixture containing the desired phenol **15**, plus a species tentatively identified by its mass spectrum as aldehyde **19**. The aldehyde could arise by loss of ethanol and enolization of the side chain carbons.

Gigg and Warren[20] reported that a mixture of mercuric chloride

and mercuric oxide in acetone/water readily cleaved prop-1-enol ethers in the presence of acid labile groups; also, benzyl ether bonds were shown to be stable under the prescribed reaction conditions. [This hydrolysis procedure may, however, fail with a polymer substrate since insoluble reagents, such as HgO in aq. acetone, are generally ineffective.[21]] Mercuric oxide is present to scavenge the hydrochloric acid generated during the hydrolysis. Other acid scavengers, such as pyridine, are known to inactivate mercuric chloride.[22,23] Model **6** was treated with TTPPR/Dabco, followed by contact with $HgCl_2$ or with the mixture $HgCl_2$/HgO. In both cases deallylation occurred in good yield. No side products were observed when HgO was present. Surprisingly, very little aldehyde (<10%) was found in the absence of HgO.

The allyl protected heterogeneous model **8** was, therefore, treated with TTPPR/Dabco, followed by $HgCl_2$. The extent of allyl group removal was qualitatively determined by FTIR. After two treatments, the allyl signals were effectively minimized; a strong hydroxyl signal was concomitantly observed, confirming that the free phenol had been generated. Analysis by ^{13}C-NMR[5] also showed that the allyl groups had been removed. The $HgCl_2$ reaction liquor contained no lignin model or lignin model degradation products, indicating that the model-polymer linkage had not hydrolyzed during the process.

Heterogeneous Model Loading Determination

Two approaches were taken in determining the quantity, or loading, of the lignin-like model on the polymer support. A loading of 1.33 mmol of model per gram of resin (mmol/g) was determined from the weight gain of the resin during the initial coupling step of the heterogeneous synthesis. The gravimetric method provides only an es-

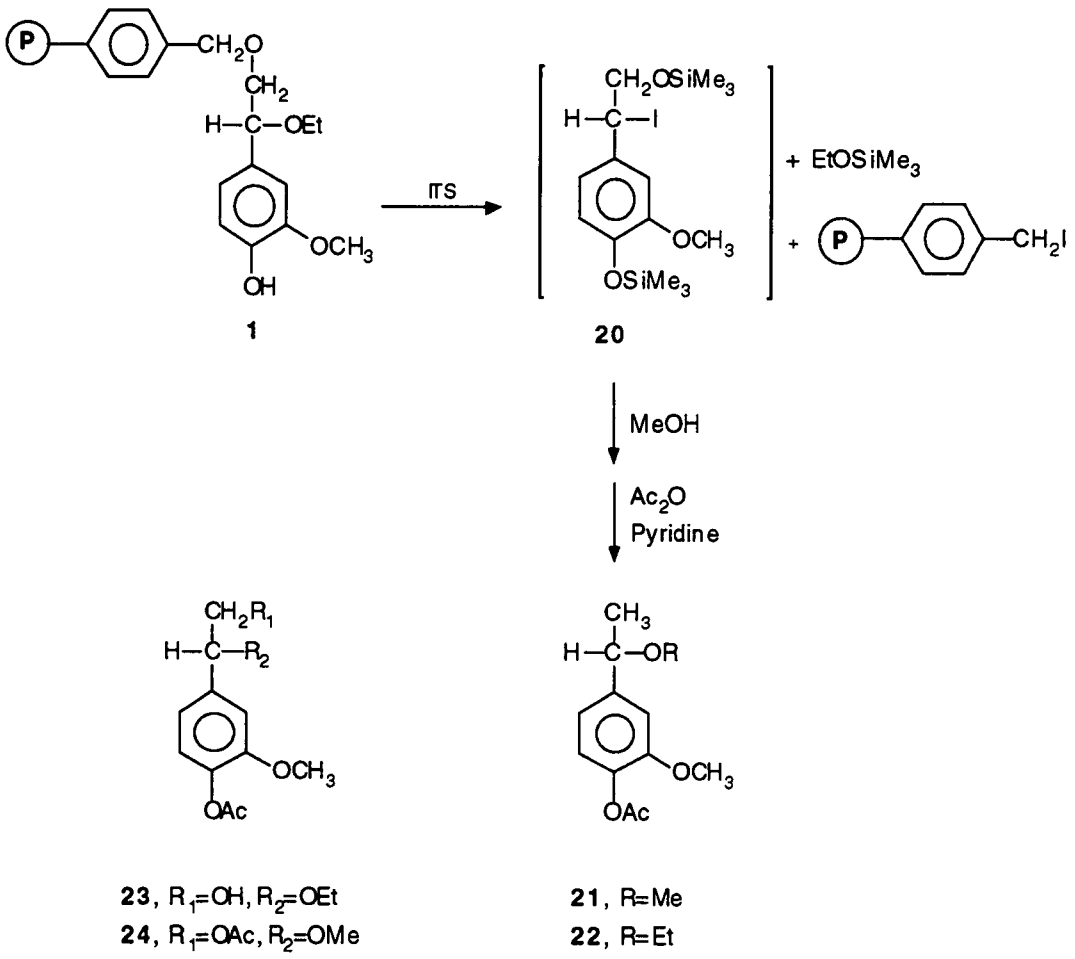
timate of the quantity of model on the polymer.[10]

The second approach involved quantifying by gas chromatography (GC) the amount of model released into solution when the model-to-polymer benzyl ether linkages were cleaved with iodotrimethylsilane (ITS).[5] This method also provided further structural proof that the intended model had been successfully prepared. The loading value obtained by the ITS technique was 0.83 ± 0.03 mmol/g. Analysis of the ITS treated resin by FTIR showed that some of the model was not removed, since residual C-O signals were observed. However, a strong benzyl iodide signal was apparent, indicating that a majority of the model had been cleaved from the support.

The discrepancy between the gravimetric and ITS loading values has been explained[5] in terms of limited accessibility in the ITS case. That is, a portion of the bound lignin models resides in regions of the macroporous resin which are inaccessible to the ITS. Model units that cannot be reached by ITS should also be inaccessible in a poorer solvent system such as aqueous alkali. The ITS loading value then is representative of the quantity of model which would most likely be accessible to the pulping reagents.

Compound **21** (Scheme 3) was identified as the soluble cleavage product after treatment of the heterogeneous model **1** with ITS. Compound **20**, resulting from cleavage of both benzyl ether linkages, was assumed to be an intermediate in the ITS reaction. When the reaction was quenched with methanol, the α-iodo group of **20** could be displaced by methanol to give **21**. Quenching the reaction with ethanol resulted in the analogous α-ethoxy compound (**22**). Treatment of soluble α-ethoxy model **15** with ITS also gave **21**, confirming that the desired model was successfully coupled to the polymer support. Compounds **23** and **24** were also observed (11 and 6% relative to **21**) in the ITS reactions. The mechanism for conversion of **1**, or **15**, to **21**

Scheme 3

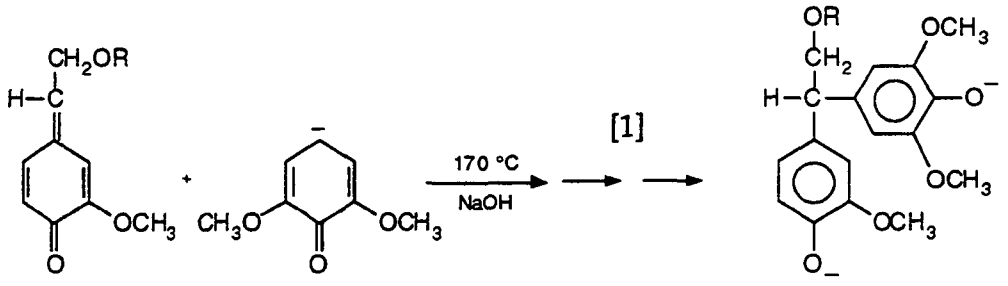


was not studied; a possible explanation is that the functional groups on the α- and β-carbons are lost simultaneously, giving a styrene structure which then adds alcohol.

Alkaline Condensation Reactions

Equation 1 outlines the two reactions of interest, namely a comparison of the extent of condensation between a soluble phenol (**3**) with two quinone methides, soluble QM **25** and insoluble QM **2**. Syringol (**3**), the phenol selected for study, should be fairly reactive and unhindered at its C-4 anionic site. The condensation product of the C-4

anion of **3**$^-$ with the QMs will be referred to as a C1-Cα dimer in keeping with lignin nomenclature. The soluble QM **25** was derived from **27**, which was prepared by benzylation of α-ethoxy precursor **6**, followed by removal of the allyl protecting group.

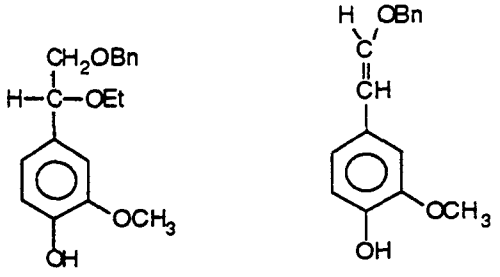


25, R = Bn
2, R = BnP

3

26, R = Bn
4, R = BnP
29, R = H

Soluble model **27** was heated at 170°C with three equivalents of syringol (**3**) in a weak alkaline solution. After the standard methylation work-up,[6] the samples were analyzed by GC and GC/MS. A relatively high yield (64%) of C1-Cα dimer **26** was detected at 15 min; over 85% of the starting material (**27**) had been consumed. A low yield of a vinyl ether **28** was detected, along with lesser amounts of several unidentified products. Extending the cook to 40 min decreased the relative level of vinyl ether present but otherwise had no major effect.



27 **28**

A test of heterogeneous QM model **1** for C1-Cα dimer formation was conducted under the same conditions as the solution-phase trial; a

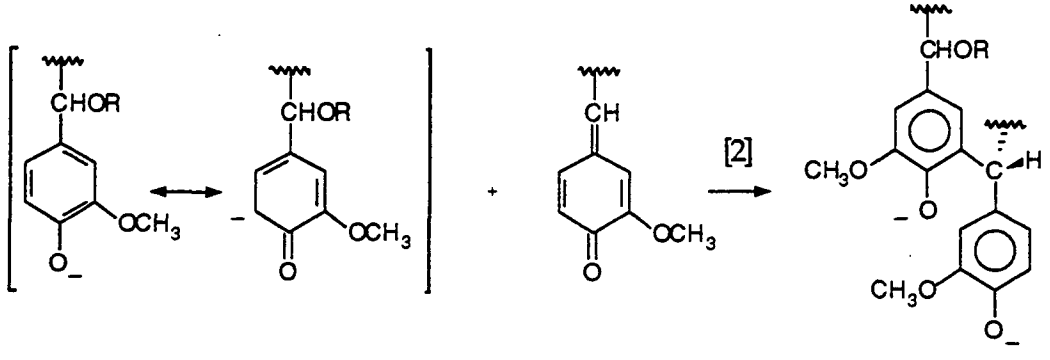
40 min sample was examined, since the rate of the heterogeneous reaction was projected to be slow. Analysis of the cooking liquor revealed that the level of syringol, relative to an internal standard, was much higher than in the soluble model case. This result indicated that the extent of condensation, as anticipated, was less. No detectable levels of a polymer-cleaved model were observed in the reaction liquor.

Treatment of the soluble C1-Cα dimer **26** with ITS led to C_β-debenzylation (compound **29**), while treatment of the reacted resin with ITS did not release **29** into solution. Obviously, the C1-Cα dimer **4** had not formed in the resin case. The level of ITS-released unreacted bound model decreased from an initial loading of 0.83 to 0.43 mmol/g. [It should be noted that the ITS method cannot distinguish between those units of bound model which have or have not undergone an alkali induced α-ethoxide/hydroxide exchange.] Only one new species, an apparent Claisen rearrangement of a residual allyl unit,[6] was observed in minor quantities in the ITS resin-treated liquor.

Likewise, the FTIR spectrum of the reacted resin was very similar to that of an unreacted sample, with the exception of stronger hydroxyl (3600-3100 cm^{-1}) and weaker aliphatic ether (1100 cm^{-1}) absorbances. The noted changes in signal intensity are probably a result of conversion of α-ethoxy to α-hydroxyl groups via addition of NaOH to heterogeneous QM intermediates. Generation of a weak unassigned olefinic signal at 1649 cm^{-1} was also observed. Weak α- and β-carbon signals in the ^{13}C-NMR spectrum of the unreacted starting material (**1**) precluded use of this technique for analyzing the reacted resin.

The low reactivity of the heterogeneous model towards the soluble phenol could be due to steric factors which prevent proper access to the QM, preference for side chain vinyl ether formation, entropy and polyelectrolyte effects, and/or intraresin condensation.

A possible route for an intraresin condensation is the reaction of a C5-anion of one bound appendage with a bound QM (Eq. 2). Intraresin condensation would effectively increase the degree of crosslinking therefore limiting the accessibility of the ITS reagent. This would account in part for the incomplete recovery of reaction products or starting material. The limited ITS accessibility and requirement that two benzyl ether bonds be cleaved in a product such as **29** could explain why no self-condensation dimer was observed.



[~~~ = to polymer]

29

Vinyl ethers, similar to **28**, generated by abstraction of a Cβ–proton,[2] have been observed as major products in other soda cooked model systems.[24, 25] A substantial degree of benzyl ether bond cleavage was observed when 4-benzoxyphenol was exposed to ITS for 25 min at room temperature; a result which shows that a benzyl ether attached to an unsaturated carbon is reactive towards ITS. Therefore, vinyl ethers should have been observed in the reaction product mixture had they been formed on the resin to a significant extent.

In an attempt to validate the intraresin condensation and vinyl ether hypotheses, we conducted a control cook of soluble model **27** in 0.050M NaOH for 15 and 40 min at 170°C. No C5-Cα dimer was identified in the product mixture; this result suggests that the formation of a C5-Cα dimer via intramolecular self-condensation on the resin

would be of low probability. The intraresin condensation theory (Eq. 2) cannot, however, be totally disregarded since the local concentration of supported model is higher than in the soluble system. A close proximity of immobilized appendages may foster intraresin reactivity.

The control test also did not support the vinyl ether proposal. A moderate amount of vinyl ether **28** was observed at the early time period; by the end of the cook the level had significantly decreased. The major product, at approximately 32%, was the starting material which had undergone an α-ethoxide/hydroxide exchange. In addition to the vinyl ether, several other minor components, whose structures could not be positively confirmed, were detected.

A likely scenario, in light of the results from the solution phase control test, may be that the modified polystyrene network effectively creates an environment in which the bound QM is shielded from the syringol nucleophile thus inhibiting heterogeneous dimer formation. The two-phased system therefore behaves as in the homogeneous control where the starting material is slowly consumed yielding an assortment of minor compounds which cannot readily be removed from the resin.

Efforts to promote heterogeneous condensation were made by modifying the reaction conditions. All endeavors were unsuccessful and led to lower recoveries, after treatment with ITS, of starting material. The conditions employed were (a) increasing the reaction time under current conditions (0.05M NaOH, three eq. of syringol) to two hours, (b) raising the base concentration, while maintaining three eq. of syringol, to 1.00M, and (c) using ten eq. of syringol which required an increase in alkali concentration to 0.10M.

In spite of low returns of starting material, no other GLC signals associated with reaction products were prevalent. Resin morphology changes could account for the nonquantitative recovery of starting

material or products, as was the case in an earlier system.[6] It is doubtful, however, that such changes would exclude the presence of heterogeneous products to the degree observed.

Several efforts were made to ensure complete removal of reacted and unreacted bound model from the phenol-treated resin. A second extended (15 hr) application of ITS to a once treated resin yielded only a trace of starting material. Another method known to cleave heterogeneous benzyl ether bonds, acetolysis, was also investigated. Acetolysis did not work efficiently with a previous lignin model,[5] but did with a supported carbohydrate.[8] Tests on soluble model **27** were successful; the benzyl ether bond was quantitatively cleaved without excessive model degradation. The subsequent acetolysis of an ITS treated resin, however, yielded only minor quantities of the starting material.

Reasons for the failure of the ITS and acetolysis methods to remove reacted model from the resin are not clear. The FTIR spectrum of an ITS resin showed a weak benzyl iodide signal at 1155 cm^{-1} which is consistent with the visible lack of released material. A complimentary SEM-EDS analysis indicated that the distribution of iodine across the resin was still homogeneous. The impotency of the ITS and acetolysis methods lends support to the intramolecular self condensation hypothesis in which overall reagent accessibility could be limited due to a higher degree of intraresin crosslinking.

CONCLUSIONS

A polymer-supported lignin model, which contained a simple guaiacyl-type appendage capable of forming a QM under alkaline pulping conditions, was prepared and characterized. Condensation products were not observed when the heterogeneous QM was reacted

with an alkaine solution of 2,6-dimethoxyphenol at high temperature. Reaction of the corresponding soluble QM with the soluble phenol under identical conditions yielded high amounts of C1-Cα dimer. It appears that steric constraints or internal cross linking may be prohibiting the potential two-phased interactions.

EXPERIMENTAL

A description of the specific instrumentation, the elemental analyses, the determination of model loading by the ITS method, and the reagents/solvents have been previously detailed.[5] Silica gel 60 (70-230 mesh ASTM) was employed as the stationary phase in all column chromatography isolations.

The polystyrene support (Amberlite XE-305), the synthesis of the polymer-supported benzyl iodide (**7**), and the general acetylation method were described in an earlier report.[5]

α-Bromo-3-methoxy-4-hydroxyacetophenone (9) - The bromoketone **9** was prepared according to the method reported by Dimmel and Shepard.[12] The bromoketone, which was isolated as a purple solid that contained residual dioxane, could be recrystallized (53% recovery) in chloroform/pet ether (2:3): mp 78.5-81.5°C (lit. 74-75°C,[16] 78-79°C[26]). Crystallization was not required since the crude bromoketone led to pure product, in a moderate yield, in the next step.

α,4-Diacetoxy-3-methoxyacetophenone (10) - The method of Ferrari and Casagrande was used.[13] Crude α-bromoacetophenone (**9**), 21.5 g (72.4 mmoles), which contained residual dioxane,[12] was stirred in 73 mL of freshly distilled acetic anhydride and 113 mmols (11.1 g) of dry potassium acetate. After gently refluxing for 15 min, the mixture was poured over 500 mL of ice-water, the resulting layers separated and the aqueous layer extracted twice with 50 mL of chloroform. The combined

organic layers were washed with 2x100 mL of water, dried over sodium sulfate (Na_2SO_4), and concentrated. The residue was then dissolved in 150 mL of boiling abs. ethanol, filtered through carbon, and cooled to give light yellow crystals (12.1 g, 63%): mp. 77.5-78.5°C (lit.[13] 77-78°C); IR (mull) cm^{-1} 1760 (ArOAc), 1725 (ROAc), and 1675 (RCOAr); ^{1}H-NMR ($CDCl_3$) δ 2.22 (s, 3, RO<u>Ac</u>), 2.32 (s, 3, ArO <u>Ac</u>), 3.88 (s, 3, OC<u>H</u>$_3$), 5.29 (s, 2, C<u>H</u>$_2$), 7.12 (d, J = 8.1 Hz, 1, C_5-H), and 7.42-7.56 (m, 2, $C_{2,6}$-Ar<u>H</u>); MS *m/e* (%) 266 (3, M^+), 224 (29), 151 (100), 123 (10), and 43 (25).

α,4-Dihydroxy-3-methoxyacetophenone (11) - Diacetate **10** (10.0 g, 37.6 mmol) was suspended in 150 mL of anhydrous methanol, containing a 1.2 molar excess (45.5 mL) of 0.99<u>M</u> sodium methoxide in methanol. After 25 min at room temperature, the reaction mixture, which had turned dark and contained a white solid, was neutralized with 1<u>M</u> HCl, and taken to dryness under reduced pressure. The residue was slurried with decolorizing carbon in warm methanol, filtered, and reduced in volume. The product, 5.31 g (78%) of yellowish crystals, was isolated after recrystallization from methanol: mp 160-162.5°C (lit.[13] 159-160°C); IR (mull) cm^{-1} 3450-3050 (OH) and 1675 (RCOAr); ^{1}H-NMR (d_6-DMSO) δ 3.83 (s, 3, OC<u>H</u>$_3$), 4.71 (s, 2, C<u>H</u>$_2$), 6.88 (d of d, J = 7.1 and 1.7 Hz, 1, C_5-H), 7.43 (s, 1, C_2-H), and 7.48 (d of d, J = 7.6 and 2.0 Hz, 1, C_6-Ar<u>H</u>), the hydroxyl protons were not readily apparent; MS *m/e* (%) 182 (11, M^+), 151 (100), 123 (21), and 108 (11).

1-(3'-Methoxy-4'-hydroxyphenyl)-1,2-ethanediol (12) - The glycol was prepared by a sodium borohydride reduction of **11** according to the general method of Nonni.[14] Five grams (27.4 mmol) of **11** was dissolved in 500 mL of abs. ethanol. Sodium borohydride (10.4 g, 274 mmol) was then added to the stirring solution over a 90 min period. The solution was protected from moisture, stirred for an additional 12 hr, and then quenched with the dropwise addition of glacial acetic acid until effervescing stopped. Upon standing, the mixture thickened and

a solid appeared. The mixture was filtered and the retained white residue washed with 2x150 mL of abs. ethanol. The filtrate and washes were reduced in volume to yield a yellowish colored solid.

The boric oxides generated during the reaction made isolation of the glycol difficult; however, a column chromatography procedure proved effective. The isolated solid was dissolved in a minimal amount of methanol and passed through a short, large diameter, silica gel 60 column with dichloromethane (500 mL) followed by 25% methanol/dichloromethane as eluents. The oily solid which was obtained from the column was slurried in 100 mL of hot ethyl acetate and filtered. The resulting filtrate was reduced in volume yielding an orange oil which was purified by column chromatography (eluent: 5% methanol in dichloromethane). A final yield of 3.66 g (72%) of a light yellow oil was obtained: IR (neat) cm^{-1} 3600-3000 (OH), no carbonyl signals were observed; ^{1}H-NMR of acetylated glycol **13**, ($CDCl_3$) δ 2.06 (s, 3, RO<u>Ac</u>), 2.11 (s, 3, RO<u>Ac</u>), 2.30 (s, 3, ArO<u>Ac</u>), 3.83 (s, 3, O<u>CH</u>$_3$), 4.24-4.36 (d of d of d, J = 11.9, 8.1, and 3.8 Hz, 2, <u>CH</u>$_2$), 6.01 (d of d, J = 8.1 and 3.8 Hz, 1, <u>CH</u>), 6.96 (d, J = 8.5 Hz, 1, $C_{6'}$-H), 6.97 (s, 1, $C_{2'}$-H), and 7.03 (d, J = 8.5 Hz, 1, $C_{5'}$-H); the mass spectrum was obtained as a silated (BSA) derivative (**14**) and was consistent with the data reported by Nonni,[14] MS *m/e* (%) 400 (1, M^+), 385 (2), 297 (100), 147 (6), and 73 (25).

2-Ethoxy-2-(3'-methoxy-4'-hydroxyphenyl)ethan-1-ol (15) - In oven-dried glassware and under a nitrogen atmosphere, glycol **12** (4.1 g, 22.2 mmol) was dissolved in 200 mL of abs. ethanol. Five equiv. (111 mL) of anh. 1.0<u>M</u> HCl in ethanol was added. The solution was shaken under a blanket of nitrogen for 24 hr, neutralized with 4<u>M</u> aq. Na_2CO_3, and filtered. The filtrate and 2x100 mL of abs. ethanol rinses were combined, diluted with 100 mL of water, and extracted with CH_2Cl_2 (3x50 mL). The organic extract was washed with water (1x100 mL), dried over Na_2SO_4, and evaporated to give a yellow oil. A yield of 2.74

g (58%) of a white solid was obtained after crystallization from toluene: mp 94.0-96.5°C; IR (mull) cm^{-1} 1090 (C-O-C); ^{1}H-NMR ($CDCl_3$) δ 1.21 (t, J = 7.0 Hz, 3, $CH_2C\underline{H}_3$), 2.31 (s, 1, O<u>H</u>, exchangeable in D_2O), 3.35-3.69 (m, 4, $OC\underline{H}_2CH_3$, $C\underline{H}_2OH$), 3.90 (s, 3, $OC\underline{H}_3$), 4.33 (d of d, J = 8.5 and 3.9 Hz, 1, C<u>H</u>), 5.68 (s, 1, O<u>H</u>, exchangeable in D_2O), 6.80 (d, J = 8.1 Hz, 1, $C_{5'}$-H), 6.83 (s, 1, $C_{2'}$-H), and 6.89 (d, J = 7.9 Hz, 1, $C_{6'}$-H); MS *m/e* (%) 212 (6, M^+), 181 (100), 153 (49), 151 (17), 125 (33), 93 (52), and 65 (16). The following spectrum was obtained from the acetylated ethoxide (**18**): ^{1}H-NMR ($CDCl_3$) δ 1.21 (t, J = 7.0 Hz, 3, $CH_2C\underline{H}_3$), 2.08 (s, 3, RO<u>Ac</u>), 2.31 (s, 3, ArO<u>Ac</u>), 3.40-3.52 (m, 2, $C\underline{H}_2CH_3$), 3.84 (s, 3, $OC\underline{H}_3$), 4.12-4.21 (d of d of d, J = 11.0, 7.8, and 4.3 Hz, 2, $C\underline{H}_2OAc$), 4.51 (d of d, J = 7.6 and 4.2 Hz, 1, C<u>H</u>), 6.91 (d, J = 8.0 Hz, 1, $C_{5'}$-H), and 6.97 (s, 1, $C_{2'}$-H), 7.01 (d, J = 8.0 Hz, 1, $C_{6'}$-H). The change in the chemical shift values for the protons on the β-carbon from 3.5 to 4.2 ppm upon acetylation indicated that the β-carbon was not etherified by treatment with acidic ethanol. The mass spectra of the minor products (**16**, **17**) from the etherification were as follows: MS *m/e* (%), **16**, 240 (5, M^+), 212 (2), 195 (18), 181 (42), 167 (13), 153 (16), 137 (62), 122 (17), 103 (100), 94 (14), 93 (19), 75 (69), and 47 (45); and **17**, 332 (25, M^+), 150 (100), and 135 (17).

2-Ethoxy-2-(3'-methoxy-4'-allyloxyphenyl)ethan-1-ol (6) - A nitrogen atmosphere, oven-dried glassware, and dry solvents were used prior to quenching. The ethoxide **15** (2.98 g, 14.0 mmol) was dissolved in 150 mL of 1:2 benzene/dimethylformamide (DMF) and added dropwise to a stirred suspension of 34.6 mg (14.0 mmol) of sodium hydride in 40 mL of 1:1 benzene/DMF. After 30 min, distilled allyl bromide (2.42 mL, 28.0 mmol), dissolved in 50 mL of benzene, was added over a period of 30 min. Stirring was continued for 24 hr during which time the solution changed in color from blue to yellow. The reaction was quenched by the addition of 30 mL of 1<u>M</u> methanolic sodium methoxide, stirred an additional 30 min, diluted with 100 mL

of water, and the two phases separated. The aqueous layer was extracted with CH_2Cl_2 (3x50 mL). The combined organic/CH_2Cl_2 phases were washed with 100 mL of water, dried over Na_2SO_4, and evaporated under high vacuum to yield a yellow oil. The crude material was purified by column chromato-graphy (eluent: 1% methanol/dichloromethane) resulting in 3.09 g (88%) of a light yellow oil: IR (neat) cm^{-1} 995, 925 ($CH=CH_2$); ^{1}H-NMR ($CDCl_3$) δ 1.21 (t, J = 7.0 Hz, 3, $CH_2C\underline{H}_3$), 2.40 (s, 1, O$\underline{H}$, exchangeable in D_2O), 3.36-3.69 (m, 4, $C\underline{H}_2CH_3$, $C\underline{H}_2OH$), 3.88 (s, 3, $OC\underline{H}_3$), 4.35 (d of d, J = 8.5 and 4.0 Hz, 1, Ar$C\underline{H}$), 4.60 (d of t, J = 5.4 and 1.4 Hz, 2, $ArOC\underline{H}_2$), 5.35 (d of d of q, J = 17.3, 10.5, and 1.4 Hz, 2, $=C\underline{H}_2$), 6.03-6.13 (d of d of t, J = 17.3, 10.5, and 1.4 Hz, 1, $C\underline{H}=$), and 6.80-6.87 (m, 3, Ar-H); ^{13}C-NMR ($CDCl_3$) ppm 15.3 (q, $CH_2\underline{C}H_3$), 55.9 (q, OCH_3), 64.3 (t, $\underline{C}H_2CH_3$), 67.2 (t, $\underline{C}H_2OH$), 69.9 (t, $ArO\underline{C}H_2$), 82.4 (d, Ar$\underline{C}$H), 109.8 (d, C_2), 113.1 (d, C_5), 118.0 (t, $=\underline{C}H_2$), 119.2 (d, C_6), 131.8 (s, C_1), 133.3 (d, $\underline{C}H=$), 147.7 (s, C_4), and 149.1 (s, C_3); MS *m/e* (%) 252 (13, M^+), 221 (100), 193 (16), 151 (28), 123 (14), 105 (10), and 93 (10).

Anal. calcd. for $C_{14}H_{20}O_4$ (%): C, 66.64; H, 7.99; O, 25.37. Found: C, 66.38; O, 7.96; O, 25.66.

Polymer-supported 2-ethoxy-2-(3'-methoxy-4'-hydroxyphenyl)-1-ethanol (1) - Sodium hydride (0.263 g, 10.6 mmol) was stirred under anhydrous conditions in 25 mL of tetrahydrofuran (THF). The allyl-protected lignin model **6**, dissolved in 75 mL of THF, was added drop-wise; stirring was continued for another 1 hr. Iodomethylated polys-tyrene resin **7** (4.51 g, 11.0 mmol) was then added. The resulting suspension was stirred for 5 days. The resin was isolated by filtration, washed with 4x200 mL of THF, extracted in a Soxhlet apparatus with THF for 12 hr, followed by hexane for 13 hr, and dried under reduced pressure at 40°C to yield 5.40 g of a light yellow resin. An analysis of the reaction liquor showed only lignin model **6** to be present indicating that the model was stable under the imposed coupling conditions. The

following FTIR signals, either new or enhanced (*) relative to the iodomethylated resin **7**, were attributed to the presence of the supported lignin model: 2970 (aliphatic C-H stretch), 1512* (C=C ring str.), 1263 and 1224 (Ar C-O str.), 1160, 1134, 1103,* 1021* (aliphatic C-O str.), 996 and 929 (=C-H bend), 843 and 810 cm^{-1} (Ar-H bend). The elemental analysis (in duplicate) was as follows: C, 72.26; H, 6.98; O, 11.29; I, 9.32.

The residual benzyl iodide groups on heterogeneous intermediate **8** were inactivated by converting them to benzyl methyl ethers. An excess of sodium methoxide in methanol (140 mL of a 1.1M solution) was added to a slurry of the resin in THF. After 3 days, the resin was isolated by filtration, washed with 6x100 mL each of methanol, acetone and THF, extracted in a Soxhlet apparatus with hexane for 8 hr, and dried in vacuo at 40°C. The FTIR showed no significant change from its precursor. The resin was also characterized by high resolution ^{13}C-NMR as previously detailed:[5] ($CDCl_3$) ppm 15.6 ($OCH_2\underline{C}H_3$), 40.4 (polystyrene $\underline{C}H$), 40-47 (polystyrene $\underline{C}H_2$), 56.3 (OCH_3), 64.6 ($\underline{C}H_2CH_3$), 69.8 ($ArO\underline{C}H_2$, $Ar\underline{C}H_2$, $ArCH\underline{C}H_2$), 80 ($Ar\underline{C}H$), 113 (broad, $C_{2',5'}$), 117.9 ($=\underline{C}H_2$), 128.3 (polystyrene Ar, $C_{1'}$), 133.5 ($-\underline{C}H=$), 149 (broad, polystyrene, $C_{3',4'}$), the signal for $ArCH_2O\underline{C}H_3$ is presumably at 56 ppm. The elemental analysis showed a significant loss in the amount of residual iodine: C, 77.74; H, 7.63; O, 12.38; I, 1.94.

Etherified resin **8** was suspended in a warm solution of tris-(triphenylphosphine)rhodium(I) chloride (0.925 g, 1.0 mmol) and 1,4-diazabicyclo[2.2.2]octane (0.449 g, 4.0 mmol) in 250 mL of 7:3:1 ethanol/benzene/water. The stirring reaction mixture was gently refluxed for 10 hr. The gray colored, cooled resin was isolated by filtration, washed with 5x100 mL each of chloroform, THF, and hexane, and then dried at 40°C under reduced pressure. A slurry of the resin in 55 mL of an acetone-water mixture (10:1), containing 1.69 g (6.22 mmol) of $HgCl_2$, was shaken for 2 hr. The resin was isolated by filtration,

washed with 5x100 mL of water, acetone, and ether, and dried at 40°C under vacuum. The isomerization and mercuric chloride cleavage steps were repeated a second time. After the second $HgCl_2$ treatment, the resin was extracted for 12 hr with hexane and dried. No cleaved model was detected in the liquors from the reaction solutions. The FTIR, relative to intermediate **8**, showed a strong broad hydroxyl signal at 3600-3200 cm^{-1} and virturally none of the allyl signals at 996 and 929 $cm.^{-1}$ Minor changes were observed in the C-O stretch region (approx. 1224 to 1134 cm^{-1}). The high resolution ^{13}C-NMR of **1** showed greatly reduced signals at 70, 118, and 134 ppm which confirmed that the allyl groups were effectively removed. No iodine or phosphorous was detected in the elemental analysis: C, 75,28; H, 7.11; O, 12.08.

The mass spectrum, *m/e* (%), for aldehyde **19**, which was obtained as a significant side product (48%) when the isomerized starting material **6** was treated with dilute HCl in acetone, was as follows: 166 (31, M^+), 137 (100), 122 (19), and 94 (10).

1-Methoxy-1-(3'-methoxy-4'-hydroxyphenyl)ethane (21) - Under anhydrous conditions, 0.47 mL (3.30 mmol) of iodotrimethylsilane was added to 50 mg (0.24 mmol) of α-ethoxide **15** dissolved in 10 mL of acetonitrile. The mixture was shaken occassionally for 30 min, quenched by the addition of 6 mL of anhydrous methanol, followed by 2.5 mL of pyridine, and concentrated under reduced pressure at 40°C. The residue was washed with 2x5 mL of anh. MeOH, dried, and treated with 7 mL of acetic anhydride, 5 mL of pyridine, and 300 mg of anhydrous sodium acetate. The acetylation mixture was quenched after 24 hr by the addition of cold water (50 mL) and extracted with 3x10 mL of dichloromethane. The organic extract was washed with 15 mL of 1M HCl, followed by 3x15 mL of water. The extract was dried (Na_2SO_4) and evaporated to yield 68 mg (98%) of yellow oil: ^1H-NMR ($CDCl_3$) δ 1.43 (d, J = 6.5 Hz, 3, $CHC\underline{H}_3$), 2.31 (s, 3, $ArO\underline{Ac}$), 3.24 (s, 3, $CHOC\underline{H}_3$), 3.84, (s,

3, ArOC$\underline{H}_3$), 4.28, (q, J = 6.5 Hz, 1, ArC$\underline{H}$), 6.85 (d of d, J = 8.1 and 1.8 Hz, 1, $C_{5'}$-H), 6.95 (d, J = 1.7 Hz, 1, $C_{2'}$-H), and 6.99 (d, J = 8.0 Hz, 1, $C_{6'}$-H,); ^{13}C-NMR ($CDCl_3$) ppm 20.7 (q, $\underline{C}H_3C$=O), 24.0 (q, CH$\underline{C}H_3$), 55.9 (ArO$\underline{C}$H-$_3$), 56.6 (q, CHO$\underline{C}H_3$), 79.4 (d, Ar$\underline{C}$H), 109.8 (d, $C_{2'}$), 118.5 (d, $C_{6'}$), 122.5 (d, $C_{5'}$), 138.9 (s, $C_{1'}$), 142.5 (s, $C_{4'}$), 151.2 (s, $C_{3'}$), and 169.1 (s, $\underline{C}$=O); MS *m/e* (%) 224 (4, M^+), 182 (17), 167 (100), 153 (32), 152 (15), 151 (33), 135 (10), 121 (12), 119 (12), 91 (23), 79 (14), 77 (17), and 43 (29).

The mass spectra for **22** , **23** and **24**, were *m/e* (%): **22**, 238 (6, M^+), 196 (31), 181 (100), 153 (28), 151 (26), 125 (13), 93 (12), 91 (10), and 43 (16); **23**, 254 (2, M^+), 223 (2), 181 (6), 149 (3), 137 (6), 75 (100), and 43 (3); **24**, 282 (1, M^+), 240 (3), 209 (6), 180 (4), 167 (100), 152 (7), 151 (7), and 43 (11).

1-Ethoxy-1-(3'-methoxy-4'-hydroxyphenyl)-2-benzyloxyethane (27) - Under anhydrous conditions, 171 mg (1.2 eq.) of sodium hydride was slurried in DMF at 45°C. After 10 min, allyl-protected compound **6** (1.45 g, 5.75 mmol, 1 eq.), dissolved in 50 mL of DMF, was dripped into the sodium hydride slurry. Benzyl bromide (2.73 mL, 4 eq.) in 20 mL of DMF was then slowly added to the reaction mixture which had been stirring for 60 min. The solution was maintained at 45°C for 6.5 days, quenched by carefully adding 46 mL (8 eq.) of 1$\underline{M}$ sodium methoxide in methanol, stirred for 3 hr while cooling to room temperature, diluted with water (200 mL), and extracted with chloroform (2x100 mL). The organic extract was dried (Na_2SO_4) and evaporated under high vacuum at 43°C. Analysis of the product mixture by GC showed that the starting material had not been completely consumed.

The crude product was benzylated a second time using similar conditions. Analysis of the resulting product mixture revealed that most, but not all, of the residual starting material (**6**) had been consumed. The benzylated product was isolated by back-to-back column chromatographies; the first with 20% ethyl acetate/toluene, the second with 1% ethyl acetate/dichloromethane, followed by 1% ethyl acetate/

1% methanol/dichloromethane to yield 1.01 g (51%) of a light yellow oil: ^{1}H-NMR ($CDCl_3$) δ 1.05 (t, J = 6.8 Hz, 3, $OCH_2C\underline{H}_3$), 3.27, 3.28 (2 q, J = 7.0 Hz, 2, $OC\underline{H}_2CH_3$), 3.35 (d of d, J = 10.4 and 4.1 Hz, 1, $CHC\underline{H}_AH_B$), 3.51 (d of d, J = 10.4 and 7.6 Hz, 1, $CHCH_A\underline{H}_B$), 3.69 (s, 3, $OC\underline{H}_3$), 4.28 (d of d, J = 7.6 and 4.1 Hz, 1, $C\underline{H}CH_AH_B$), 4.34 (d, J = 12.2 Hz, 1, $OC\underline{H}_MH_NAr$), 4.44 (d of t, J = 5.4 and 1.4 Hz, 2, $ArOC\underline{H}_2$), 4.48 (d, J = 12.3 Hz, 1, $OCH_M\underline{H}_NAr$), 5.17 (d of d of q, J = 17.3, 10.5, and 1.4 Hz, 2, $=C\underline{H}_2$), 5.88-5.96 (d of d of t, J = 17.3, 10.5, and 1.4 Hz, 1, $C\underline{H}=$), 6.64-6.70 (m, 3, Ar-H), and 7.09-7.17 (m, 5, Ar-H of benzyl); MS *m/e* (%) 342 (4, M^+), 221 (100), 193 (21), 165 (11), 137 (14), 133 (11), 124 (12), 105 (16), 91 (56), 77 (10), and 65 (11).

The allyl ether protecting group was removed from the intermediate product by refluxing 783 mg (2.29 mmol, 14.6 eq.) of the benzylated intermediate obtained above for 28 hr in 60 mL of ethanol/benzene/water (7:3:1), containing 1 eq. (145 mg) of TTPPR and 4 eq. (71 mg) of Dabco. Upon cooling, the reaction mixture was diluted with water (30 mL) and extracted with CH_2Cl_2 (3x30 mL). The residue from evaporation of the CH_2Cl_2 was dissolved in 25 mL of 10:1 acetone/water containing 747 mg (1.5 eq.) of yellow HgO; finally, $HgCl_2$ (627 mg, 1 eq.) in 10 mL of the acetone/water solution was added over a period of 5 min. The resulting mixture was shaken for 1 hr, filtered through ceilite to remove the HgO, and reduced in volume. The residual material was diluted with 30 mL of CH_2Cl_2, washed with 10 mL of sat. aq. KI, dried (Na_2SO_4), and evaporated. A white solid (0.50 g, 72%) was obtained after purification of the residue by column chromatography (eluent: 20% ethyl acetate/toluene followed by a second column of 1% methanol/dichloromethane): mp 75-77°C; ^{1}H-NMR ($CDCl_3$) δ 1.15 (t, J = 7.0 Hz, 3, $OCH_2C\underline{H}_3$), 3.42, 3.43 (2 q, J = 7.0 Hz, 2, $OC\underline{H}_2CH_3$), 3.50 (d of d, J = 10.4 and 4.1 Hz, 1, $CHC\underline{H}_AH_B$), 3.66 (d of d, J = 10.4 and 8.6 Hz, 1, $CHCH_A\underline{H}_B$), 3.85 (s, 3, $OC\underline{H}_3$), 4.38 (d of d, J = 7.6

and 4.1 Hz, 1, C<u>H</u>CH$_A$H$_B$), 4.45 (d, J = 12.3 Hz, 1, OC<u>H</u>$_M$H$_N$Ar), 4.58 (d, J = 12.3 Hz, 1, OCH$_M$<u>H</u>$_N$Ar), 5.55 (s, 1, O<u>H</u>, exchangeable in D_2O), and 6.73-6.83 (m, 3, Ar-H), 7.20-7.26 (m, 5, Ar-H of benzyl); ^{13}C-NMR ($CDCl_3$) ppm 15.4 (q, OCH$_2$<u>C</u>H$_3$), 55.9 (q, O<u>C</u>H$_3$), 64.4 (t, O<u>C</u>H$_2$CH$_3$), 73.4, 74.8 (2 t, CH<u>C</u>H$_2$ and Ar<u>C</u>H$_2$), 81.2 (d, Ar<u>C</u>H), 109.0 (d, C$_{2'}$), 114.0 (d, C$_{5'}$), 120.1 (d, C$_{6'}$), 127.5 (d, C$_4$ of benzyl), 127.7 (d, C$_{3,5}$ of benzyl), 128.3 (d, C$_{2,6}$ of benzyl), 131.9 (s, C$_{1'}$), 138.4 (s, C$_1$ of benzyl), 145.3 (s, C$_{4'}$), and 146.6 (s, C$_{3'}$); MS *m/e* (%) 302 (3, M$^+$), 181 (69), 153 (43), 152 (28), 151 (33), 137 (20), 133 (30), 125 (29), 93 (34), 91 (100), 77 (22), and 65 (40).

<u>Anal</u>. calcd. for $C_{18}H_{22}O_4$ (%): C, 71.50; H, 7.33; O, 21.17. Found: C, 69.93; H, 7.11, O, 20.18.

Attempts to prepare **27** by selectively adding[12] a benzylate anion to α-bromoacetophenone, followed by $NaBH_4$ reduction and etherification with EtOH/HCl, were unsuccessful. Unidentified products were obtained during the initial addition step.

1-(3',5'-Dimethoxy-4'-hydroxyphenyl)-1-(3"-methoxy-4"-hydroxyphenyl)-2-benzyloxyethane (26) - Model **27**, 6.3 mg (0.020 mmoles), was heated with 3 eq. of syringol (**3**) in 0.050<u>M</u> NaOH for 15 min at 170°C in a minibomb.[6] Upon cooling, the contents of seven identical prepared and reacted minibombs were emptied into a common container, along with 2x3 mL of 0.050<u>M</u> NaOH rinses of each minibomb. The reaction mixture was acidified to pH 5 with 5<u>M</u> acetic acid, and extracted with CH_2Cl_2 (4x10 mL). The CH_2Cl_2 was evaporated and the residue purified by column chromatography (eluent: 1% MeOH/CH_2Cl_2) to yield 26.6 mg (45%) of yellow oil, C1-Cα dimer **26**: ^{1}H-NMR ($CDCl_3$) δ 3.80 (s, 3, OC<u>H</u>$_3$"), 3.81 (s, 6, OC<u>H</u>$_3$'), 4.18 (t, J = 7.1 Hz, 1, ArC<u>H</u>), 4.60 (d, J = 3.4 Hz, 2, β-C<u>H</u>$_2$), 5.30 (s, 2, ArC<u>H</u>$_2$), 5.44, 5.50 (2 s, 2, OH, exchangeable in D_2O), 6.44 (s, 2, C$_{2',6'}$-H), 6.70-6.74 (m, 2, C$_{2",5"}$-H), 6.85 (d, J = 8.1 Hz,, 1 C$_{6"}$-H), and 7.26-7.39 (m, 5, Ar-H of benzyl); ^{13}C-NMR ($CDCl_3$) ppm 50.7 (d, Ar<u>C</u>H), 55.9 (q, O<u>C</u>H$_3$"), 56.3 (q, O<u>C</u>H$_3$'), 73.2 (t,

Ar$\underline{C}H_2$), 73.8 (t, β-$\underline{C}H_2$), 105.2 (d, $C_{2',6'}$), 111.2 (d, $C_{2''}$), 114.1 (d, $C_{5''}$), 120.9 (d, $C_{6''}$), 127.6 (d, C_4 of benzyl), 127.8 ($C_{3,5}$ of benzyl), 128.3 ($C_{2,6}$ of benzyl), 132.2 ($C_{1'}$), 133.5 (s, $C_{4'}$), 134.2 ($C_{1''}$), 138.2 (s, C_1 of benzyl), 144.1 (s, $C_{4''}$), 146.3 (s, $C_{3''}$), and 146.8 (s, $C_{3',5'}$); the dimer was methylated (Me_2SO_4) before MS, *m/e* (%): 438 (12, M^+), 317 (100), and 91 (35).

Soluble C1-Cα dimer **26** (13 mg, 0.032 mmol) was treated with 0.040 mL (0.14 mmole) of ITS for 25 min at room temperature. The reaction was quenched with anh. MeOH and the resulting product acetylated to give 1-(3',5'-dimethoxyphenyl)-1-(3"-methoxyphenyl)-2,4',4"-triacetoxyethane **(acetylated 29)**: MS *m/e* (%) 446 (2, M^+), 344 (40), 302 (100), 289 (44), and 43 (13).

Condensation reactions - All condensation reactions and product isolations involving soluble and insoluble QM models **27** and **1** were conducted in minibombs according to standard methods.[6] A quantity of 0.0200 mmol of **1** or **27** per bomb was employed; specific conditions are described in the text. The MS, *m/e* (%), for hydrolyzed/methylated starting material **27** and (methylated) vinyl ether **28** were as follows: 1-(3',4'-trimethoxyphenyl)-2-benzyloxy-1-methoxyethane, 302 (0.2, M^+), 181 (13), 165 (100), 137 (8), 122 (5), 107 (5), 91 (10), 77 (10), and 65 (5); 1-(3',4'-dimethoxyphenyl)-2-benzyloxyethene, 270 (18, M^+), 241 (12), 179 (100), 165 (23), 151 (65), 148 (29), 136 (13), 121 (13), 107 (14), 91 (81), 77 (15), and 65 (24). The MS of the Claisen rearranged product, 4'-acetoxy-5'-allyl-1,3'-dimethoxyphenylethane, detected in the ITS product mixture of reacted **1**, was as follows: 264 (4, M^+), 222 (33), 207 (100), 191 (16), 91 (10), and 43 (20).

Benzyl ether cleavage of model **27** via acetolysis,[8] glacial acetic acid/acetic anhydride/sulfuric acid (1:1:0.4), was nearly quantitative and led to **3'-methoxyphenyl-1,2,4'-triacetoxyethane**: MS *m/e* (%) 310 (2, M^+), 208 (34), 166 (83), 153 (100), 137 (8), 93 (14), and 43 (98).

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