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AN EXAMPLE OF DRAMATIC REACTIVITY DIFFERENCES FOR

FRAGMENTATION OF A β-ARYL ETHER BOND BY AHQ^{-2} AND SH$^-$

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ABSTRACT

A lignin model (3E) with a propanol group on the β-carbon has been heated in alkali with no additives and with NaSH and anthra-hydroquinone (AHQ) additives. The β-aryl ether bond of the model is efficiently fragmented by AHQ, but not by NaSH or simple NaOH. A competing cyclization of the propanol group with the quinone-methide of the model interferes with NaOH and NaSH fragmentation reactions. The data suggest that AHQ reacts by way of a mechanism different from that of NaSH – the AHQ by an electron transfer mechanism and the NaSH by an adduct mechanism. The reactions of β-allyl (3D) and β-propyl trityloxy (3F) models were also performed. The fragmentation efficiencies in these cases were: AHQ > NaSH > NaOH.

INTRODUCTION

The delignification of wood during alkaline (soda) pulping is aided by additives such as sodium hydrosulfide (NaSH, kraft pulping) and anthrahydroquinone (AHQ, anthraquinone pulping).[1] Primarily because of the structural complexities of lignin and lignin fragmentation products, delignification mechanisms are difficult to define. Models of lignin are often studied in order to help define possible pulping reaction mechanisms. Fragmentation of a model's β-aryl ether bond is considered to be synonymous with wood delignification.[1] Generally the models are capable of forming a key reactive lignin intermediate, a quinonemethide (QM), i.e., a structure similar to 1.
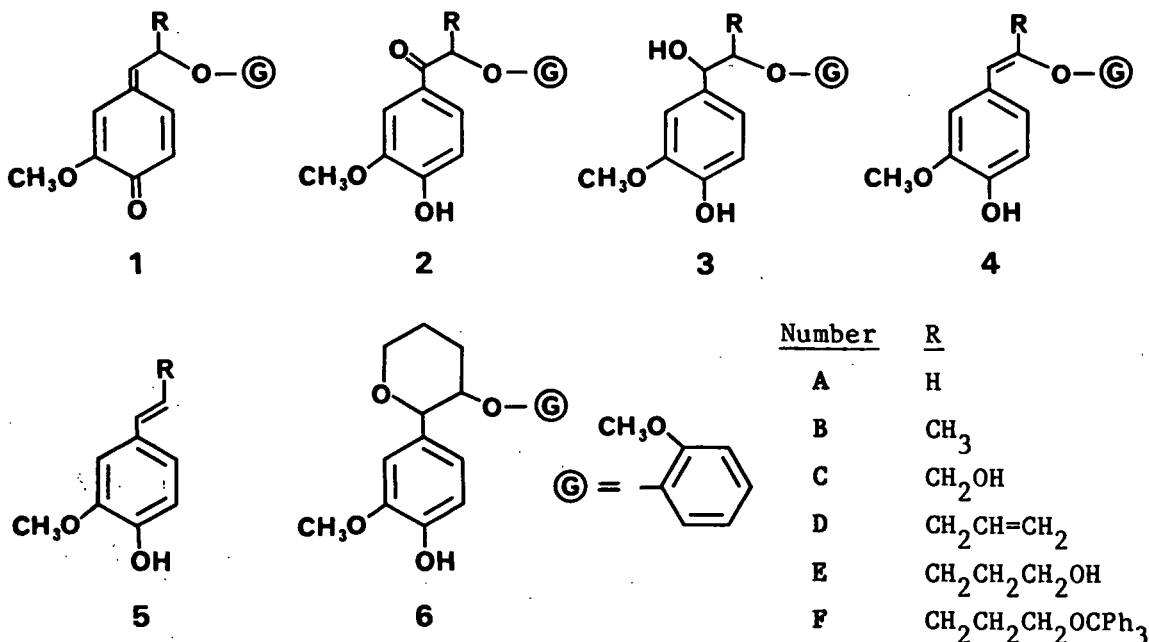
Model studies indicate that QM generation is the slow step in the additive-promoted delignification processes.[2,3] Because of this, kinetic studies often fail to provide useful mechanistic information about the nature of the additive-QM reactions.[3,4] Other complicating factors are that the additive reactions involve several steps (additions, deprotonations, eliminations, etc.) and compete with other reactions available to the QM, such as stilbene and vinyl ether formations.[3,5]

The study described herein purposely establishes a competing QM reaction in order to demonstrate the relative rates of additive-assisted delignification. The study employs model compounds which, in one respect, contain characteristic lignin groupings (α-hydroxy-β-aryl ether phenols), but, in another respect, contain atypical pentanol side chains.

RESULTS

Model Compounds

Typical delignification (model fragmentation) studies use models such as 3A-C. These models can be readily prepared by reduction or alkylation-reduction of ketone 2A.[7] Similarly, alkylation of 2A with allyl bromide gives 2D, which when reduced by NaBH$_4$ affords model 3D. Hydroboration, followed by an aqueous alkaline hydrogen peroxide treatment, converts the "allyl" model 3D to the "propanol" model 3E. The latter, upon treatment with trityl chloride (Ph$_3$CCl or simply TrCl), affords the "propyl trityloxy" model 3F.

Structures

Compounds **1**, **2**, **3**, **4**, **5**, **6**

Number	R
A	H
B	CH_3
C	CH_2OH
D	$CH_2CH=CH_2$
E	$CH_2CH_2CH_2OH$
F	$CH_2CH_2CH_2OCPh_3$

$\textcircled{G} = $ (2-methoxyphenyl)

Model Reactions

Figures 1–3 give the guaiacol (2-methoxyphenol) yield data (i.e., % fragmentation) as a function of time when models **3D–F** are heated at 150°C under soda, kraft, and soda/AHQ conditions. The degradation of the propyl trityloxy model **3F** was conducted in 29% dioxane, a solvent medium in which **3F** was soluble at room temperature. Dioxane, however, can adversely affect fragmentation yields;[8,9] an example can be seen in the data of Fig. 3.

Gas chromatography-mass spectrometric (GC-MS) analysis of the product mixtures from the degradations of allyl model **3D** showed fragmentation products, guaiacol and cis and trans styrenes **5D** (which increased with increasing time when glucose, NaSH, and AHQ were present) and starting material (which decreased with increasing time). The level of vinyl ether by-product **4D**, which was also observed, followed the order: no additive > glucose > NaSH > AHQ.

The GC-MS analysis of the product mixture from degradation of the propyl trityloxy model **3F** was incomplete because of the low volatility of the tritylated compounds. A styrene fragmentation
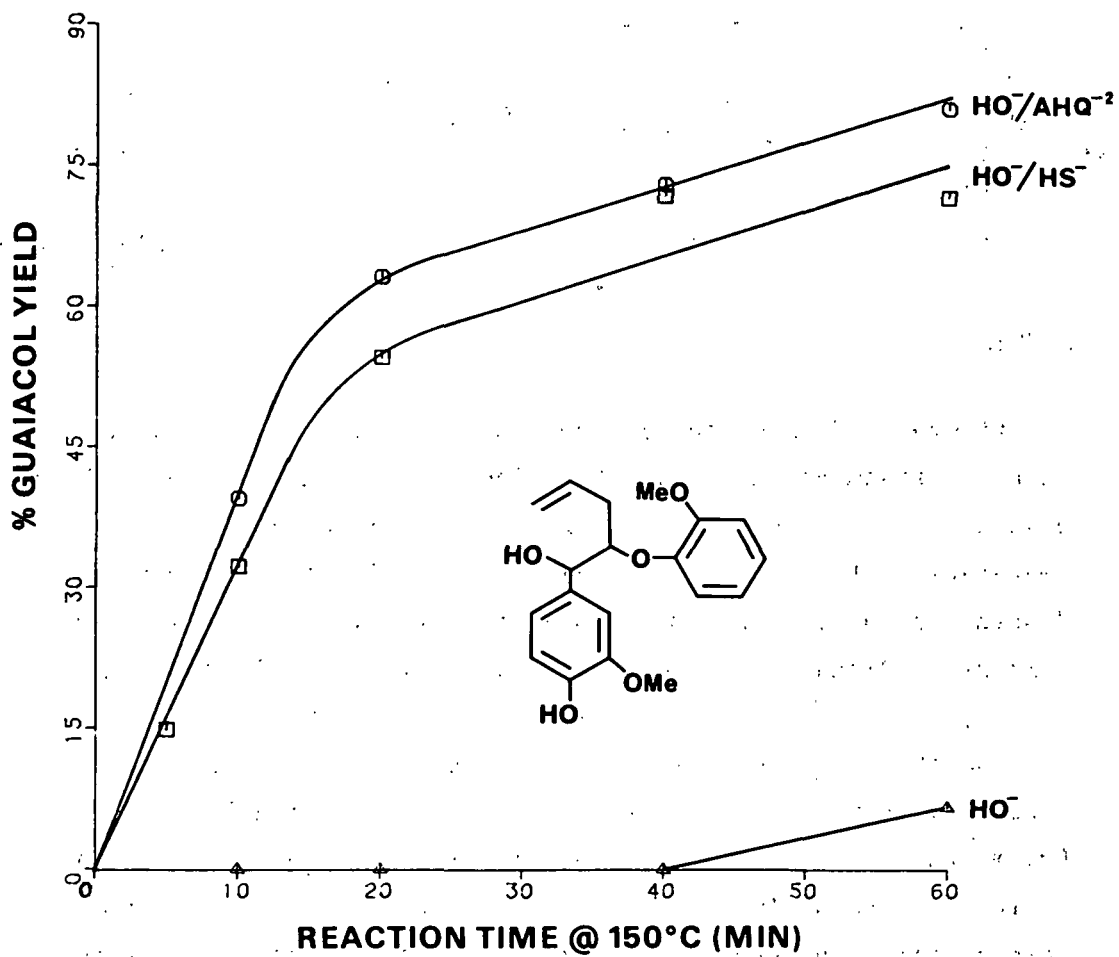
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Figure 1. Guaiacol yield as a function of time for the degradation of model **3D** at 150°C in water in the presence of 25 equiv. of NaOH, and 5 equiv. of NaSH, and 5 equiv. of AHQ (prepared from 5 equiv. each of AQ and glucose).
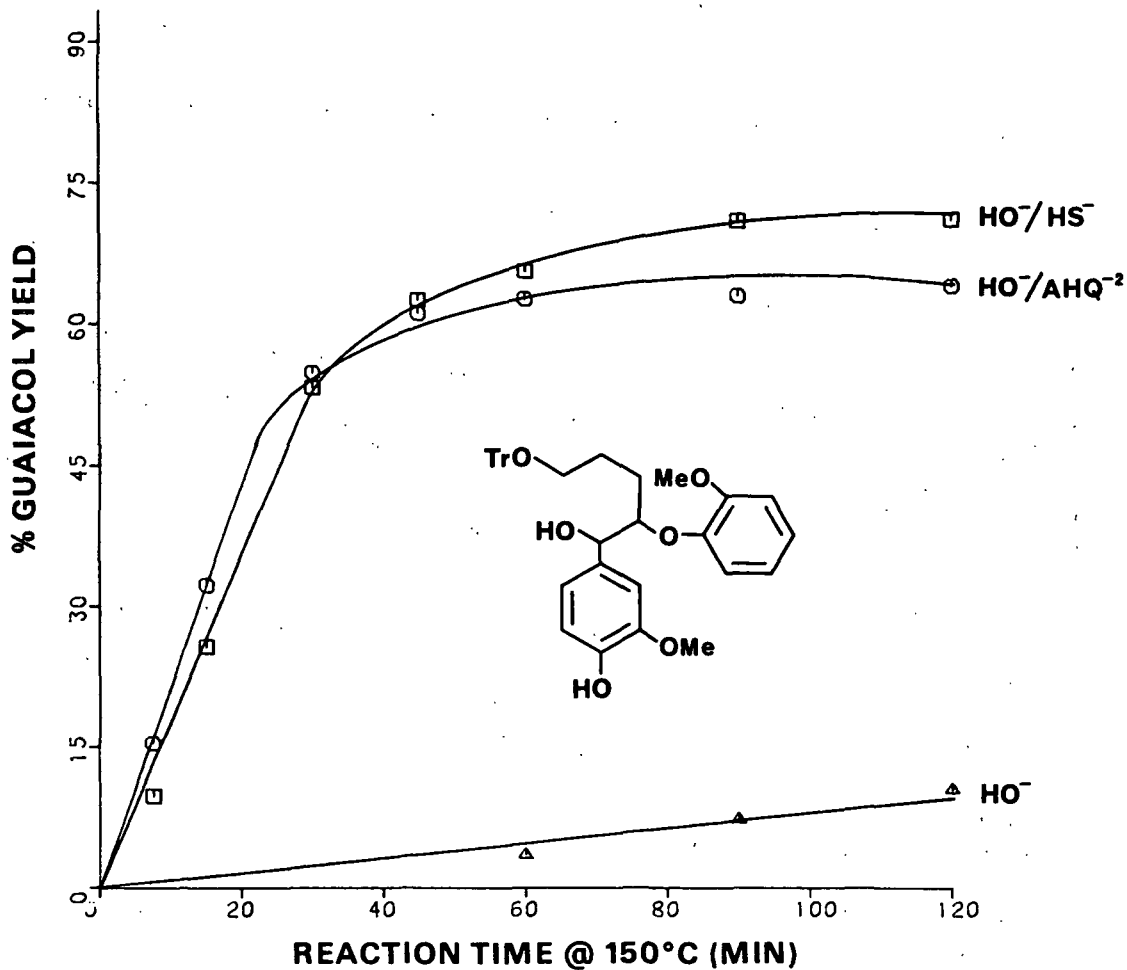
Figure 2. Guaiacol yield as a function of time for the degrada-
tion of model 3F at 150°C in 29% dioxane/water in the
presence of 25 equiv. of NaOH, and 5 equiv. of NaSH,
and 5 equiv. of AHQ (prepared from 5 equiv. each of AQ
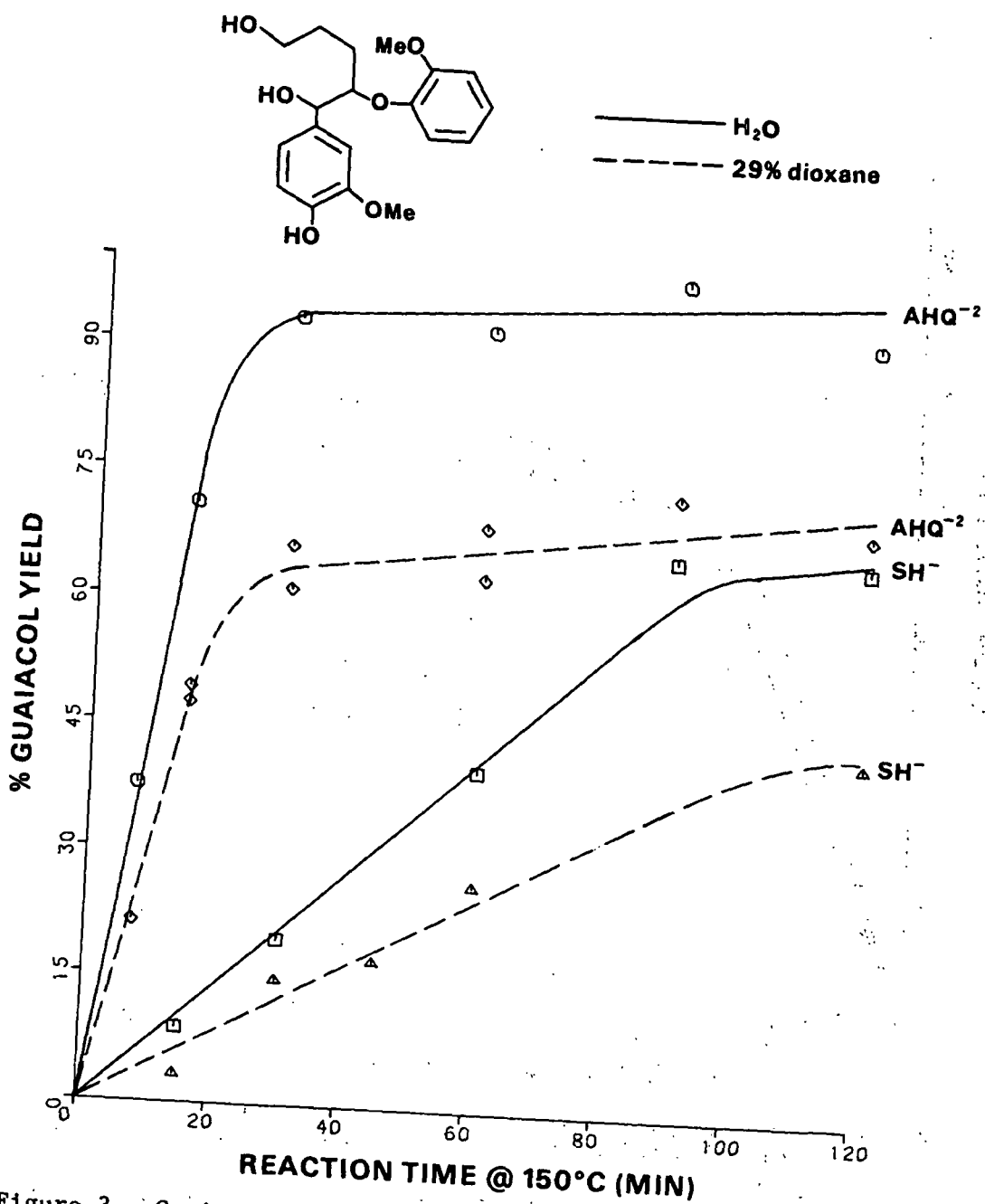and glucose).

Figure 3. Guaiacol yield as a function of time for the degrada-
tion of model 3E at 150°C in either pure water or 29%
dioxane-water in the presence of 25 equiv. of NaOH and
5 equiv. of NaSH, or 5 equiv. of AHQ (prepared from 5
equiv. each of AQ and glucose).

product 5F was, however, observed in significant amounts in additive degradation runs, but not in the simple NaOH run. Small amounts (ca. < 10%) of trityl alcohol and triphenyl methane were also observed in some of the product mixtures.

In contrast to the results with models 3D and 3F, the degradation of the propanol model 3E did not give fragmentation products under simple soda conditions and exhibited large differences in fragmentation yields for AHQ and NaSH (Fig. 3). The GC-MS analyses of additive product mixtures showed the usual loss of starting material and gain in fragmentation products, guaiacol and cis and trans styrenes 5E, with increasing time. The vinyl ether by-product 4E was not observed in any of the degradation runs of model 3E. Instead a side-chain cyclization product 6 was observed, increasing in the order: no additive > NaSH > AHQ.

The cyclized product was present in high yields at long reaction times with the NaOH degradation of model 3E. It was isolated by chromatography of the soda reaction residue and characterized by spectral means (see Experimental Section for details).

Comparative degradations of the propanol model 3E and the cyclized compound 6 were done in aqueous alkali at both 150°C and 135°C with no additives, with AHQ and with NaSH. Fragmentation was not observed in the absence of the additives. The cyclized compound fragmented, giving rise to guaiacol, when AHQ and NaSH were present (Fig. 4 and 5); the levels of fragmentation were less than that of the uncyclized model (3E). Both the cyclized model (6) and propanol model (3E) were much more reactive toward AHQ than NaSH. The differences were quite dramatic at the lower temperature of 135°C (Fig. 5).

DISCUSSION

Model degradations typically show a fast fragmentation phase and a slow phase,[3,5] such as seen in Fig. 1. This behavior is
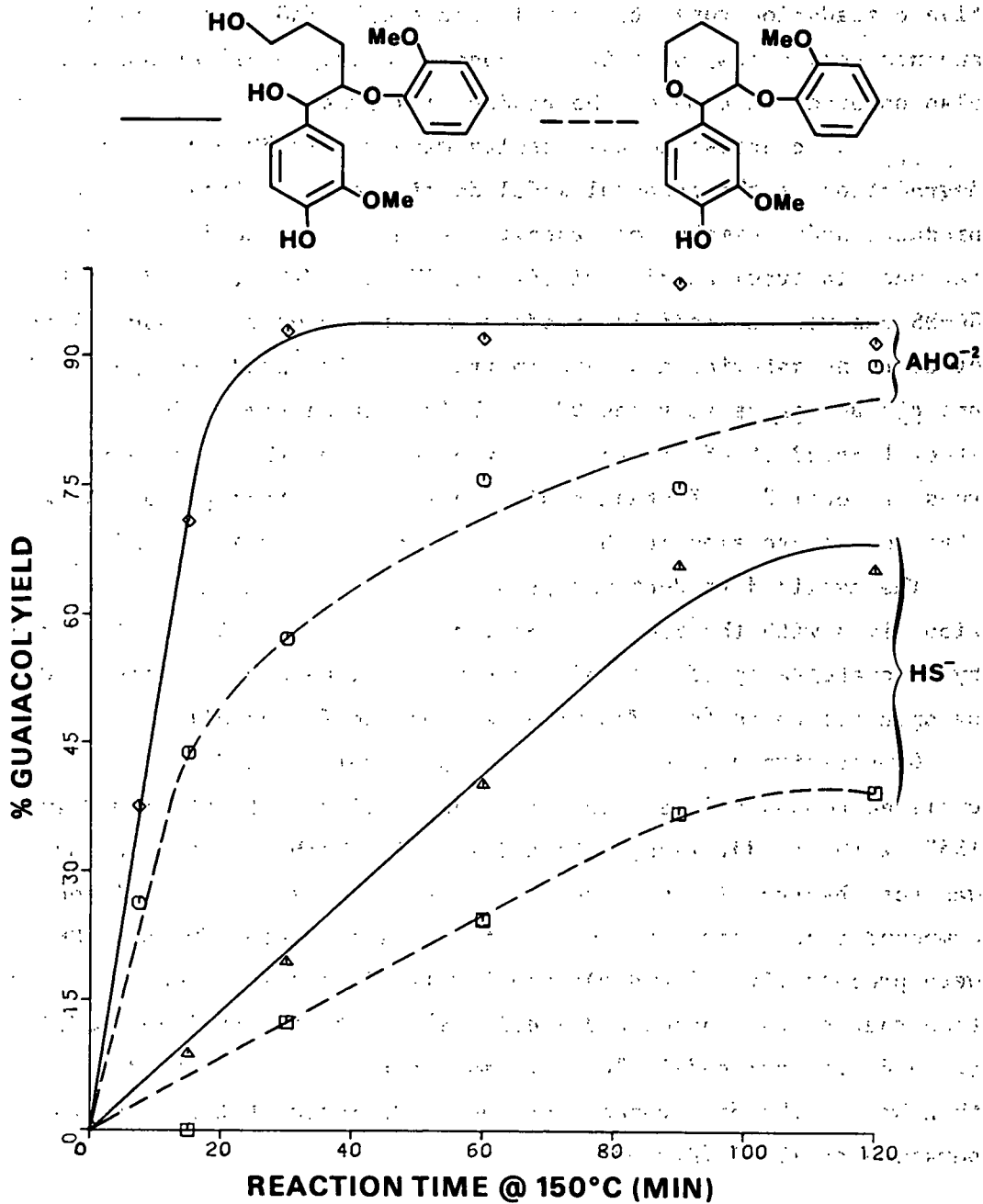
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Figure 4. Guaiacol yield as a function of time for the degrada-
tion of models 3E and 6 at 150°C in water in the pres-
ence of 25 equiv. of NaOH and 5 equiv. of NaSH, or 5
equiv. of AHQ (prepared from 5 equiv. each of AQ and
glucose).

Figure 5. Guaiacol yield as a function of time for the degrada-
tion of the models **3E** and **6** at 135°C in water in the
presence of 25 equiv. of NaOH, and 5 equiv. of NaSH or
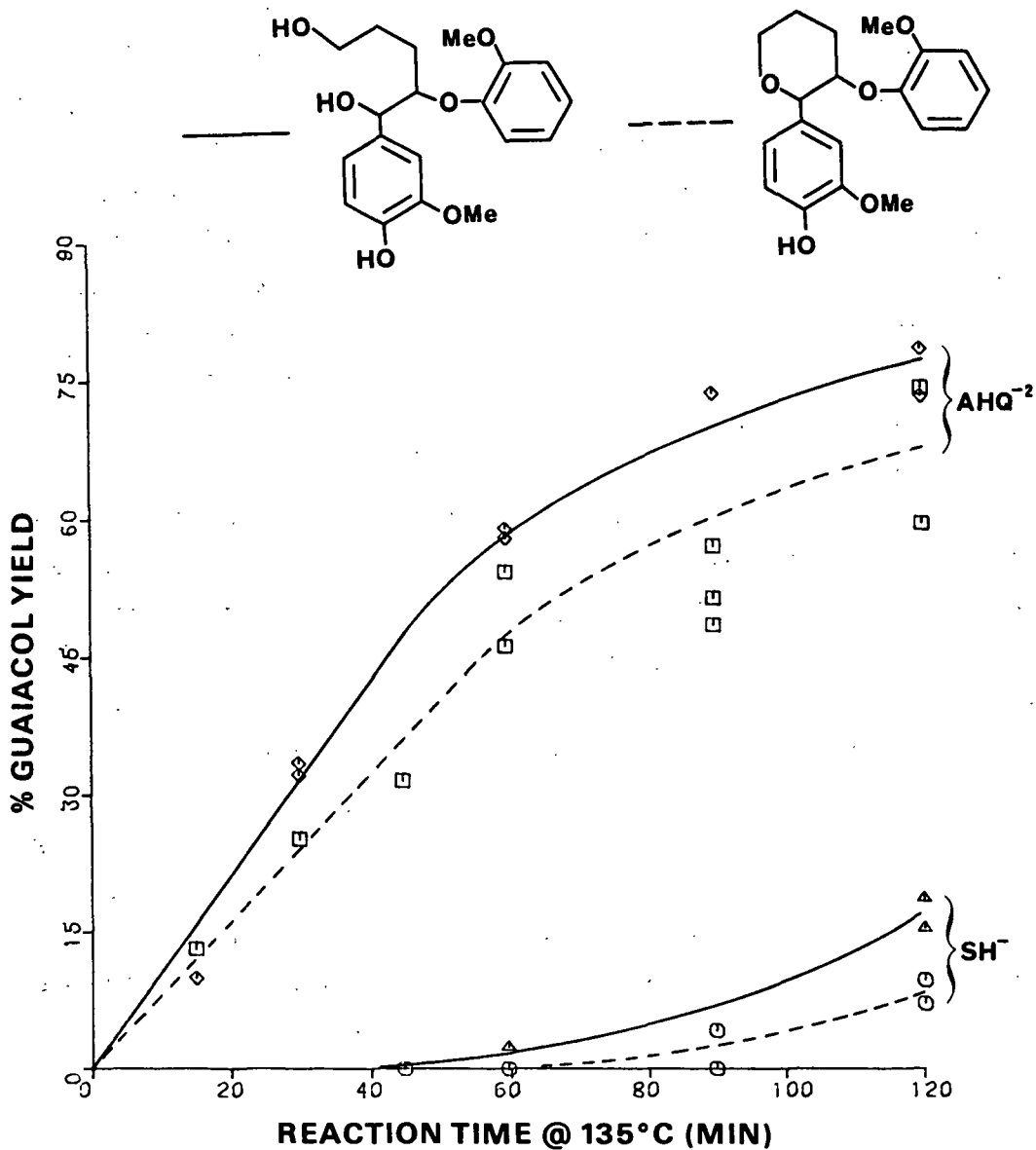5 equiv. of AHQ (prepared from 3 equiv. each of AQ and
glucose).

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indicative of competing reactions of the type shown in Scheme 1.[3,5] Initially the model is converted to fragments and vinyl ether products. The fast fragmentation process decreases when the supply of QMs diminishes. After awhile, the only supply of QMs is from the slow reversal of the vinyl ether formation reaction.[10]
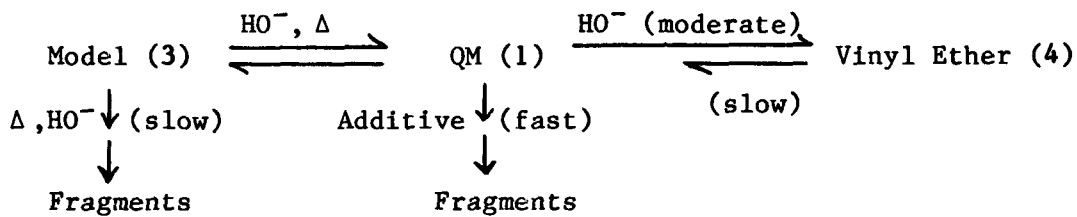
Both the allyl and propyl trityloxy models, 3D and 3F, appear to display this type of behavior. Also, each gave small, but real, amounts of fragmentation under soda conditions and similar, relatively high fragmentation yields with NaSH and AHQ. The observation here (especially at early reaction times) that AHQ gives somewhat higher fragmentation yields than NaSH agrees with earlier findings and has been interpreted to mean that AHQ is more effective at diverting QM intermediates toward fragmentation and away from nonproductive side reactions.[3]

Scheme 2 summarizes, in a qualitative manner, the degradation results with the propanol model 3E. In the absence of additives the model is efficiently converted to cyclized product 6 and fragmentation is not observed. This means that the direct fragmentation of the model is slow relative to QM formation and that intramolecular cyclization of the QM is quite fast, super- ceding other competing reactions such as vinyl ether formation.
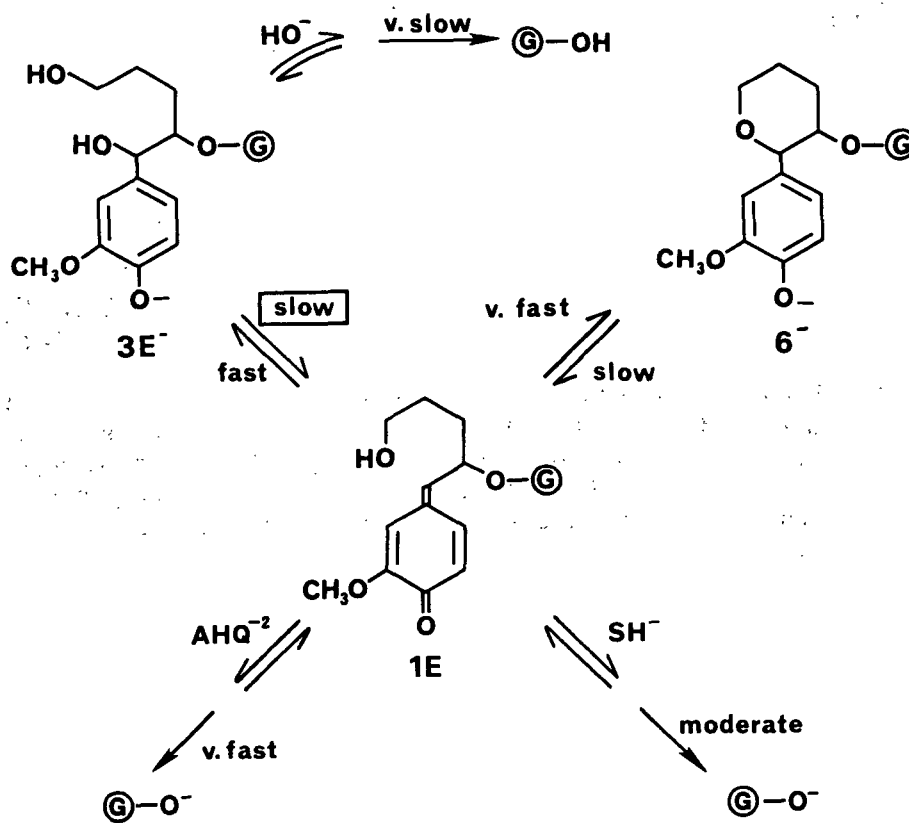
The fact that cyclized compound 6 gives significant levels of fragmentation (guaiacol) upon treatment with AHQ^{-2} or NaSH at 150°C indicates that the cyclization step is reversible. The additives can act upon the QM formed by ring opening of 6 to cause fragmentation; direct attack of additives on the cyclized material 6 to give guaiacol would be unlikely.[1,11,12]

Once formed, the QM has several reaction options, all of which regenerate an aromatic system. It is apparent from our data that the option of reacting with AHQ to give fragments is of low energy and quite favorable. The AHQ fragmentation option competes favorably with the fast side-chain QM cyclization reaction. On a relative basis, capture of the QM by SH^- and subsequent fragmen- tation is slow compared to cyclization of the QM.

SCHEME 1
Typical Model Reaction Pathways

Model (3) $\xrightleftharpoons{\text{HO}^-, \Delta}$ QM (1) $\xrightleftharpoons[\text{(slow)}]{\text{HO}^- \text{ (moderate)}}$ Vinyl Ether (4)

Δ, HO⁻ ↓ (slow) Additive ↓ (fast)

Fragments Fragments

SCHEME 2
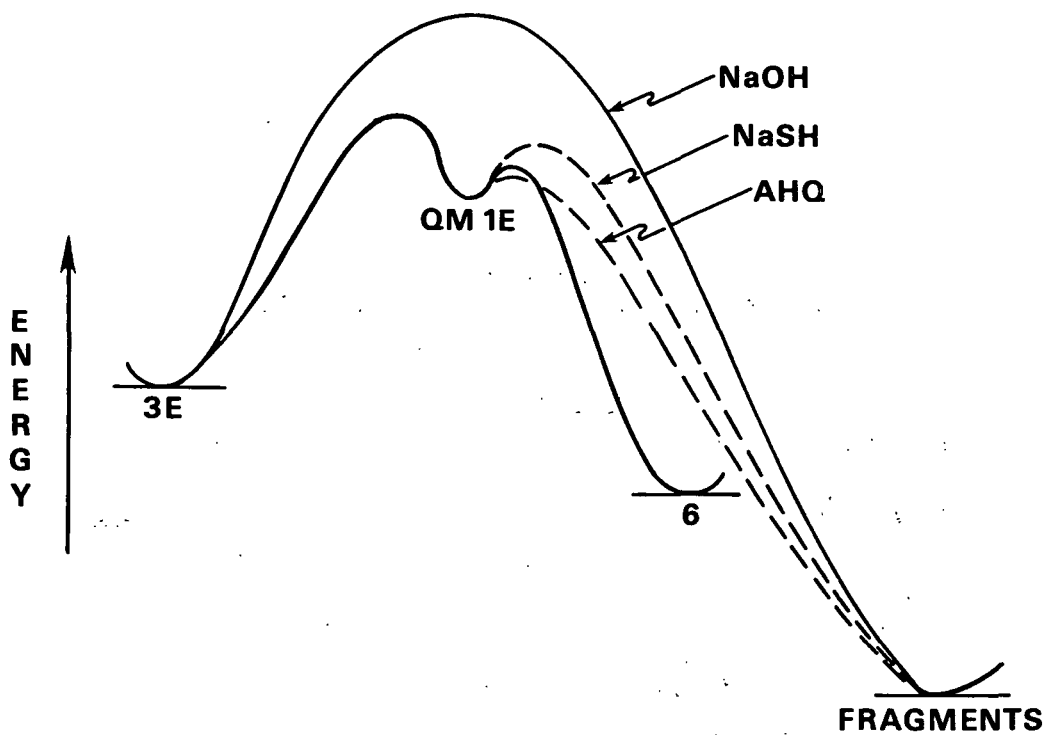### Reactions of the β-Propanol Model 3E

Figure 6. Proposed energetics for the reactions associated with model **3E**. For simplicity, the multiple steps associated with the NaOH, NaSH and AHQ fragmentation processes have been omitted and the fragmentation products are considered to have the same energies from all processes.

The qualitative interpretation presented in Scheme 2 can also be expressed by an energy diagram, Fig. 6. Fragmentation by OH⁻ is a high energy process.[5] The slow step for fragmentation by an additive (SH⁻ or AHQ⁻²) is initially QM formation from the simple model 3E.[3] After the reactions proceed for awhile and 3E has essentially been fragmented or converted to cyclized product 6, the slow step appears to be QM generation from 6. Consequently, the rates of the forward and backward steps in the cyclization process have a major impact on the extent of fragmentation possible with slower competing processes, such as the OH⁻ and SH⁻ reactions.

The reactions of the propanol model 3E, together with its competing cyclization reaction, demonstrate that AHQ⁻² is a superior additive to SH⁻ at model fragmentation. Why? Both AHQ and NaSH could be acting via "adduct" mechanisms,[1,13] with the QM-AHQ adduct (7⁻²) being either easier to form or more prone to fragment than the QM-SH adduct (9⁻²), Scheme 3.

For the QM-AHQ adduct mechanism to be superior to the QM-SH adduct mechanism, one has to argue that AHQ⁻² is a better nucleophile than SH⁻. The latter, however, is considered to be an excellent nucleophile. The subject of relative nucleophilicities of AHQ⁻² and SH⁻ is presently being studied in our laboratory.[14] The high fragmentation efficiencies exhibited by AHQ⁻² with the hindered substrates studied here and elsewhere,[4] and by bulky organometallic compounds with simple lignin models,[15] suggests that the reaction mechanisms are not of the adduct type.

Since the protons attached to thiol sulfurs are more acidic than those attached to alcoholic oxygens, the dianion intermediate 9⁻² should be more abundant than dianion intermediate 7⁻². Thus, by a combination of arguments (nucleophilicities, steric inhibition to reaction, and relative acidities), the dianion intermediate necessary for β-aryl ether cleavage should be more easily achieved with NaSH than AHQ. The questions that remain are whether the energies of the β-aryl ether elimination steps are critical to

SCHEME 3
Possible Cleavage Mechanisms of the β-Propanol Model QM 1E
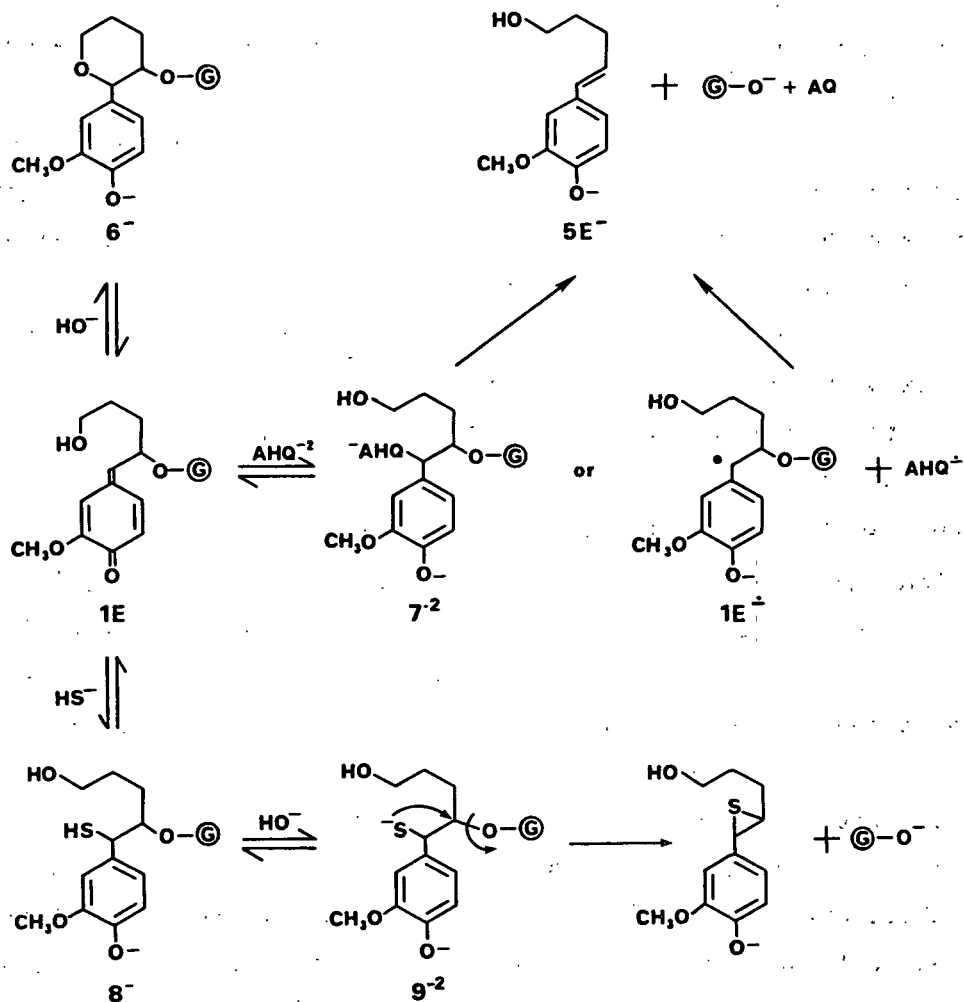
fragmentation processes and whether elimination from the QM-AHQ
adduct is more facile than from the QM-SH adduct.

The fact that AHQ and NaSH have such great reactivity dif-
ferences with the propanol model 3E indicates that AHQ is probably
acting _via_ a different chemistry than NaSH. This unique chemistry
could be electron transfer[13] between AHQ^{-2} and QM 3E, leading to
radical ion intermediates $AHQ^{\cdot-}$ and $1E^{\cdot-}$ and subsequent fragmen-
tation of the latter. Reactions of this type have been
demonstrated under idealized conditions.[16]

CONCLUSIONS

The propanol model 3E has a built-in cyclization reaction pos-
sible when its quinonemethide (1E) is formed in aqueous alkali. The
superior ability of AHQ^{-2} to fragment this model indicates that
there is a chemistry available, probably electron transfer chemistry,
which can effectively compete with the cyclization reaction. The
poor effectiveness of NaSH to induce fragmentation of 3E suggests
that its adduct mechanism does not compete well with cyclization.

With the other models, 3D and 3F, vinyl ether generation com-
petes with model fragmentation. Both AHQ and NaSH-induced fragmen-
tation appear to be of lower energy than vinyl ether generation.
The fact that AHQ^{-2} fragmentation efficiencies are higher than
that of NaSH suggests that the energy of AHQ-fragmentation is
lower than that of NaSH-fragmentation and, thus, competing reac-
tions will be less for the AHQ case. The slow step in the addi-
tive reactions and vinyl ether generation is still quinonemethide
generation. If it were not for competing reactions, the fragmen-
tation efficiencies of AHQ^{-2} and SH^{-} would be the same.

EXPERIMENTAL SECTION

The equipment,[17] guaiacol analysis by methylation and GC anal-
ysis with p-isopropylphenol as an internal standard,[5] model

degradation procedures,[3,5] and model/reagent amounts[3,5] have been previously described. Some specific details are given in the figure captions. The synthesis of the models will appear in a separate publication.[18] The model names are: 2-(2-methoxyphenoxy)-1-(3-methoxy-4-hydroxyphenyl)-4-penten-1-ol (3D), 2-(2-methoxyphenoxy)-1-(3methoxy-4-hydroxyphenyl)-1,5-pentadiol (3E), and 2-(2-methoxyphenoxy)-1-(3methoxy-4-hydroxyphenyl)-5-triphenyl-methoxy-1-pentanol(3F).

Analysis of the methylated product mixtures by GC-MS led to the tentative identification of several compounds. The identifications were based on GC elution times relative to known components of the mixtures and an interpretation of the mass spectra. The compounds tentatively identified by this procedure are listed below.

1-(3,4-Dimethoxyphenyl)-1,4-pentadiene (methylated 5D)

Two isomers of this type were observed in the reaction mixtures of the AHQ and NaSH degradations of model 3D; the two were assumed to be $\underline{cis}/\underline{trans}$ isomers of the 1,4-pentadiene type, but could be other position isomers such as 1,3 or 2,4 (conjugated) pentadienes. The two eluted at times intermediate between methylated guaiacol and dimer 3D and had nearly identical spectra: $\underline{m}/\underline{e}$ (%), 204 (100, M$^+$), 189 (74, M-CH$_3$), 174 (35, M-CH$_2$O), 173 (64, M-OCH$_3$), 158 (57, M-CH$_3$, OCH$_3$), 131 (26), 129 (44), 128 (24), 115 (32), and 91 (20).

2-(2-Methoxyphenoxy)-1-(3,4-dimethoxyphenyl)-1,4-pentadiene (methylated 4D)

This compound was most prominent in the soda degradation of 3D and eluted just prior to methylated 3D: $\underline{m}/\underline{e}$ (%) 326 (100, M$^+$), 300 (23, M-HC≡CH), 257 (30, M-HC≡CCH$_2$), 226 (21), 225 (21), 202 (34, M-HOPhOCH$_3$), 188 (23), 178 (29), 172 (29), 151 (33, diOMePhCH$_2$$^+$), and 115 (23).

1-(3,4-Dimethoxyphenyl)-5-triphenylmethoxy-1-pentene (methylated 5F)

This compound was observed in the AHQ and NaSH degradations of **3F** at 25.7 min (6 ft glass column packed with 3% OV-1 on 100-120 mesh gas chrom WHP, temperature programmed at 65° for 2 min, 2°/min to 80°, 30°/min to 285° and then hold at 285°C); $\underline{m/e}$ (%) 464 (3, M^+), 243 (100, Ph_3C^+), 221 (45, M-CPh_3), 177 (48, diOMePhCH=$CHCH_2^+$), 165 (53, PhCHPh), 151 (15, diOMePhCH$_2^+$), and 105 (26, PhC≡O^+).

1-(3-Methoxy-4-hydroxyphenyl)-2-(2-methoxyphenoxy) tetrahydropyran (6)

This compound was observed in product mixtures from high temperature alkaline degradation reactions of **3E**. Methylated **6** displayed the following mass spectrum: $\underline{m/e}$ (%) 344 (55, M^+), 221 (100, M-C_2 substituent), 220 (24, M-C_2 subst. and H), 165 (27, 3,4-diOMePhC≡O^+) and 151 (41, 3,4-diOMePhCH$_2^+$). The compound (underivatized) was also isolated from **3E** degradations as described below.

Into each of 26 small pressure vessels (bombs)[5] was placed 40 mg of **3E** and 3.5 mL of 1$\underline{M}$ NaOH, prepared from deoxygenated distilled water; the filling and sealing of the bombs was done in a glove bag under a nitrogen atmosphere. The bombs were rotated in a 135°C oil bath for 3 hrs, cooled, opened, and added collectively (along with 1$\underline{M}$ NaOH rinses of the bombs) to a separatory funnel. The solution was acidified with dilute HCl and extracted three times with $CHCl_3$. The combined $CHCl_3$ extracts were dried (Na_2SO_4) and evaporated.

The viscous liquid residue was dissolved in a small volume of CH_2Cl_2 and applied to the top of a CH_2Cl_2 slurry packed silica gel-60 column (1.5 x 60 cm). The column was eluted with 50 mL of CH_2Cl_2, 100 mL of 2.5% EtOAc/CH_2Cl_2, 200 mL of 5% EtOAc/CH_2Cl_2, and 300 mL of 10% EtOAc/CH_2Cl_2; roughly 70-10 mL fractions were

collected. Analysis by GC showed that fractions 13-20 (550 mg, 53%) were pure compound 6: $\underline{m}/\underline{e}$ (%) 330 (38, M^+), 207 (100, M-R), 206 (34, M-RH), 151 (38, $RC\equiv O^+$), 137 (57, RCH_2^+), 124 (10, RH^+), 109 (13) and 77 (14), where R is a 3-methoxy-4-hydroxyphenyl or 2-methoxyphenoxy group; ; ^{1}H-NMR (CDCl$_3$) δ 1.81 (m, 3, C$_4$-protons and one of the C$_3$-protons), 2.40 (m, 1, one of C$_3$-protons), 3.5-3.8 (m, 1, C$_2$$\underline{H}$), 3.71 and 3.80 (s, 3 and 3, OCH$_3$), 4.05 (m, 2, C$_5$-protons), 4.34 (d, J = 9.0 Hz, 1, C$_1$$\underline{H}$), 5.52 (s, 1, O$\underline{H}$) and 6.5-7.0 (m, 7, Ar$\underline{H}$) - the assignments were aided by specific proton decoupling experiments; ^{13}C-NMR (CDCl$_3$) δ 25.5 and 30.2 (t, C$_3$ and C$_4$ methylene carbons), 55.7 and 55.8 (q, O$\underline{C}$H$_3$ groups), 68.1 (t, C$_5$), 79.2 (d, C$_2$), 82.8 (d, C$_1$), 110.1, 112.3, 113.7, 117.2, 120.4, 120.5, and 121.8 (d, protonated aryl carbons), 131.6, 144.9, 145.8, 147.0 and 150.3 (s, nonprotonated aryl carbons).

ACKNOWLEDGMENTS

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