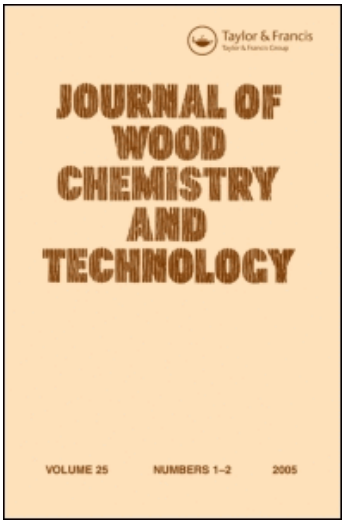

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Alkaline Pulping of Wood and Lignin Model Compounds in Aqueous Dmso

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ALKALINE PULPING OF WOOD AND LIGNIN MODEL COMPOUNDS IN AQUEOUS DMSO

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ABSTRACT

Lignin model fragmentation studies done in alkaline aqueous DMSO exhibited a high degree of β-aryl ether cleavage, a degree equal to that of a comparable soda/AQ system. Pulping studies with loblolly pine in aqueous DMSO demonstrated that DMSO accelerates delignification, but the quantities required appear impractical. Several lignin model compounds have been heated at 150°C with alkali in aqueous DMSO to give complex product mixtures containing oxidation, reduction, and methyl sulfide addition products. Low temperature reactions of DMSO and dimsyl anion with in situ generated quinonemethides afforded unique products. Reactions attributed to DMSO were not observed when an oxidized analog, dimethylsulfone, was substituted for the DMSO.

INTRODUCTION

Organic solvents are often used in conjunction with water to insure homogeneous reactions during lignin model studies. Sometimes the organic solvent plays an unexpected role, either promoting or hindering reaction. For example, Obst found that increasing the relative amounts of dioxane during degradation of an etherified lignin model compound hindered reaction by creating two phases at elevated temperatures.[1] We have found that low levels of dimethylsulfoxide (DMSO) promote the fragmentation of a model lignin compound and promote the pulping of wood. These results, along with some preliminary mechanistic studies, are described here.

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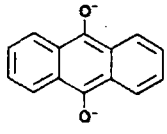
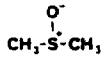
RESULTS

Lignin Model Fragmentation Studies

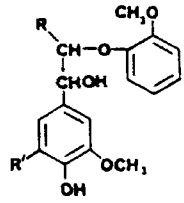
Lignin model compound 1 was heated with alkali at 153°C for 1 hour in small pressure vessels, both with and without AHQ^{-2} present, in order to ascertain what effects AHQ^{-2} had on the extent of cleavage of the β-aryl ether bond of the model. Fragmentation of this bond produces guaiacol (2). The amount of guaiacol liberated was determined by a sensitive gas chromatography-mass spectroscopy (GC-MS) technique. A known quantity of 3,5-dideuteroguaiacol was added as an internal standard prior to each reaction, and following work-up of the reaction, the ratio of guaiacol to guaiacol-d_2 was determined by selected ion monitoring (SIM) of masses 124 and 126 by GC-MS. This method of analysis allows the use of very small sample sizes (i.e., 2 mg of 1 per experiment) and should alleviate the problems associated with efficient recovery of the partially water soluble guaiacol.[2]



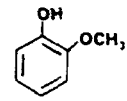
AHQ^{-2}



DMSO



1, R = CH_3, R′ = H
2, R = R′ = H
3, R = H, R′ = OCH_3
4, R = CH_2OH, R′ = OCH_3



5

The yield of guaiacol from the fragmentation of 1 with OH^- and OH^-/AHQ^{-2} varied considerably with changes in the composition of the solvent system. Figure 1 shows the variability of guaiacol yields as the solvent composition is changed from 75% dioxane to pure water to 75% DMSO. The data of Fig. 1 point out several interesting features of these degradation reactions.

Increasing the relative amounts of dioxane in the system retards the fragmentation reaction both in control and AHQ runs.

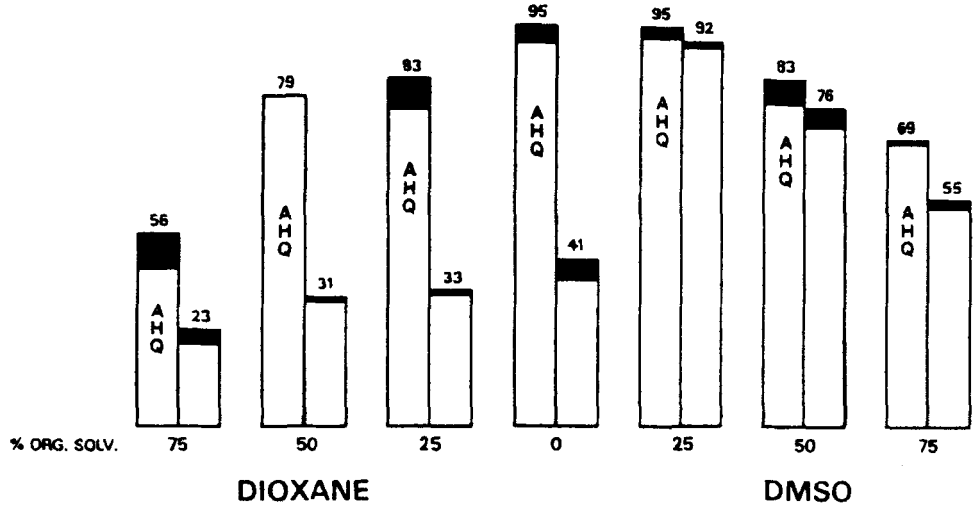


Figure 1. The percent guaiacol liberated from α-hydroxy model 1 at 153° after 60 minutes in an alkaline solution, with and without AHQ. Solid area on the top of each bar indicates the range of duplicate runs.

Our results support the conclusion of Obst[1] that water alone is a better solvent than dioxane-water mixtures for obtaining efficient model fragmentation reactions. Degradations in DMSO produced higher yields of guaiacol than those in dioxane.

The DMSO/OH^- control degradations were much better than the pure water system and were nearly as effective as the corresponding AHQ^{-2} degradations. As the level of DMSO decreased, the fragmentation efficiency of the model both increased and approached more closely that of the AHQ^{-2} case. The efficiency of 5% DMSO in aqueous alkali was indistinguishable from AHQ^{-2} in water or in water-5% DMSO mixtures. [At a 5% solvent level, the DMSO was still in large excess relative to the model. The AHQ^{-2} experiments employed three equivalents of AHQ^{-2} per equivalent of model.]

Previous model studies by Fullerton[3] (employing 2) and Sano and coworkers[4] (employing 1, 3, and 4) have demonstrated that DMSO

has a positive effect on β-aryl ether cleavage. These investigators either employed DMSO neat, in conjunction with potassium t-butoxide,[3,4] or 50-90% DMSO-water mixtures with NaOH.[3] The extent of β-aryl ether cleavage of models is often taken as an indication of wood delignification efficiencies.[5,6] Thus, the results of the model reactions suggested that dilute alkaline DMSO-water mixtures may be as good as soda-AQ for the delignification of wood.

Pulping Studies

The literature has numerous references to the use of DMSO in pulping systems in which the DMSO is the only solvent and/or in which acid catalysts are present.[4,7-14] Also, DMSO has been used in amine pulping[11b,15,16] and in pulping pretreatments.[17,18] Sweetgum has been pulped with 1N NaOH in 50% aq. DMSO and the rate of delignification was found to be faster than with other mixed solvent systems and faster than kraft pulping.[19] Our pulping studies principally concerned dilute DMSO solutions.

The rate of soda pulping of loblolly pine chips was significantly accelerated by the addition of DMSO (Table 1). In fact, pulping with soda/25% DMSO gave the same yield, kappa number, and rejects as an analogous cook with 0.1% AQ. At 75% DMSO, there was no free liquid phase after pulping; the chips were very swollen. Although the model studies' prediction was confirmed, pulping with 25% DMSO is not very practical.

The results of pulping with low levels of DMSO are given in Table 2. A DMSO level of roughly 3% based on oven-dry wood was needed to observe a significant delignification rate increase. The ineffectiveness of the first 1% DMSO may be due to its consumption by some minor wood component. Pulping with mixed systems of DMSO and AQ or sulfide indicated some complementary effects with AQ, but not with sulfide. A 3% DMSO/0.05% AQ/soda system behaved similarly to a 0.1% AQ/soda system.

Technology is available for paper mills to produce inexpensive dilute aqueous solutions of DMSO;[20] however, DMSO would have to

TABLE 1

Effects of Large Amounts of DMSO in Soda Pulping[a]

DMSO, % liquor vol.	DMSO, % o.d. wood	AQ, % o.d. wood	Total Yield, %	Screened Rejects, % o.d. wood	Screened Pulp Kappa No.
0	0	0	54.0	8.6	100.0
25	110	0	42.6	1.1	25.6
25	110	0.1	42.2	0.4	25.1
75	330	0	44.0	21.0	25.8

[a]Constant conditions: 18% Na_2O on o.d. wood, liquor-to-wood ratio 4.0, 90 minutes rise to 173°C, 120 minutes at 173°C, loblolly pine chips (air-dry).

TABLE 2

Effects of Small Amounts of DMSO in Soda Pulping[a]

DMSO, % o.d. wood	Total Yield, %	Screened Rejects, % o.d. wood	Screened Pulp Kappa No.	Carbohydrate Yield,[b] %	Lignin Yield,[c] %
0	50.6	6.2	87.1	44.0	6.61
0.2	50.8	3.4	87.2	44.2	6.65
0.4	50.1	2.8	89.5	43.4	6.73
0.8	50.5	5.9	89.8	43.7	6.80
1.6	50.7	2.7	86.4	44.1	6.57
3.2	49.4	1.3	83.1	43.3	6.16
6.4	48.5	1.2	72.5	43.2	5.28

[a]Constant conditions as in Table 1, except chips soaked in water before cooking liquor addition; final pH = 13.4 in each case.
[b]Total yield - lignin yield.
[c]Lignin yield = 0.0015 x kappa x total yield.

cost 4¢/lb to partially replace AQ at $2.40/lb. Chemical recovery of DMSO from pulping liquors would probably be costly. Thus pulping with DMSO appears impractical.

Model Product Studies

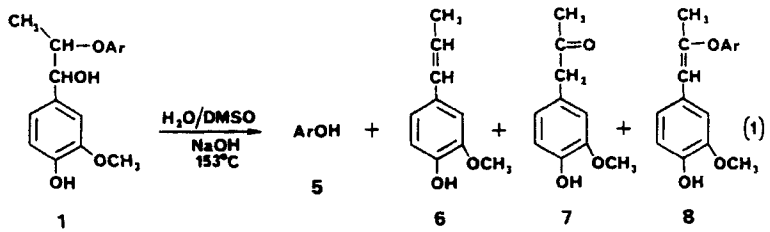
The effectiveness of DMSO in alkaline pulping systems is probably related to a chemical reaction between the DMSO and lignin. This fact is borne out by the previously described model studies and the effective concentration range of DMSO (5-25%) in the

pulping studies. Physical effects, such as the swelling of cell walls and solvation of the lignin,[21] may also play a role.

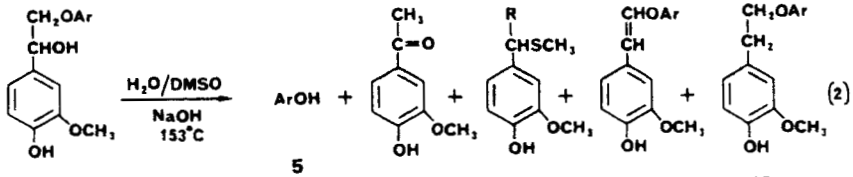
While DMSO pulping looks commercially unattractive, understanding its chemistry may provide insights into new pulping strategies. The acid catalyzed elimination of benzyl alcohol groups from dibenzyl ether structures in aq. DMSO[22] and the reactions of 3 and 4 with t-BuOK in anhydrous DMSO[4] appear to be the only previous "mechanistic" studies with DMSO and lignin models. We, therefore, briefly examined the nature of the volatile product obtained in some lignin model reactions with aqueous alkaline DMSO solutions.

Product mixtures were analyzed by GC/MS and components were assigned structures based on direct and indirect comparison to known samples or interpretation of the mass spectral data. Except for guaiacol from 1 and 2, component yields were not quantified. The odor of some of the products precluded extensive purification and quantitation attempts. The preliminary nature of this study just concerned a cursory examination of type and rough amounts of the products.

Heating lignin model 1 with aqueous DMSO/alkali at 153°C gave, besides some recovered starting material, guaiacol (5) in large amounts (Fig. 1), isoeugenol (6) in moderate amounts and ketone 7 and vinyl ether 8 in minor amounts [Eq. (1), where Ar = o-methoxyphenol]. The latter compound may not be a primary product, but rather formed by dehydration of 1 during reaction work-up and/or GC analysis. Isoeugenol is an interesting product in that it is also seen in reasonable levels with AQ pulping conditions but not soda or kraft conditions.[6]

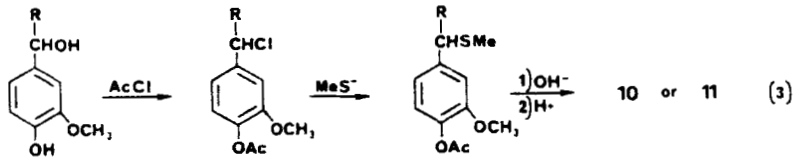


A similar degradation of model **2** gave, upon GC-MS analysis, the following product mixture: starting material, guaiacol, acetoguaiacone **9**, two sulfides **10** and **11**, vinyl ether **12**, and a component tentatively identified as **13** (Eq. 2). The fragmentation product analogous to **6**, except no β-CH_3 (i.e., **31**) was not detected; it (4-vinylguaiacol) is prone to be lost by polymerization side reactions. The identification of minor component **13** was based on its GC retention time and MS signals at m/e 274 (molecular ion) and 137 (benzyl ion from C_α-C_β cleavage).



2 **5** **9** **10**, R = H; **11**, R = CH_3 **12** **13**

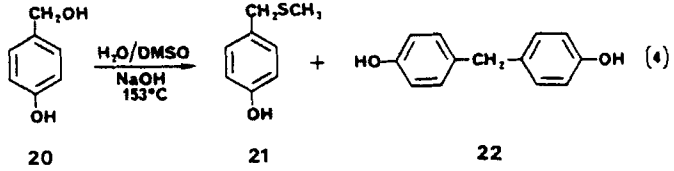
The two sulfides were unexpected products. Confirmation of their structures was provided by independent syntheses and comparison of GC retention time and MS characteristics. The syntheses were accomplished by the set of reactions outlined in Eq. (3).

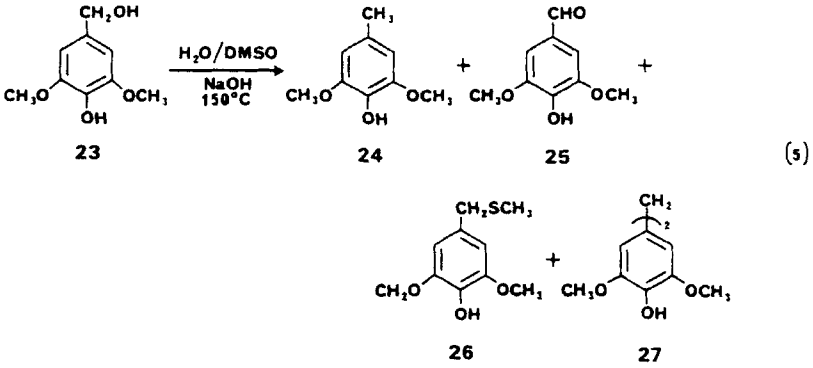


14, R = H; **15**, R = CH_3 **16**, R = H; **17**, R = CH_3 **18**, R = H; **19**, R = CH_3

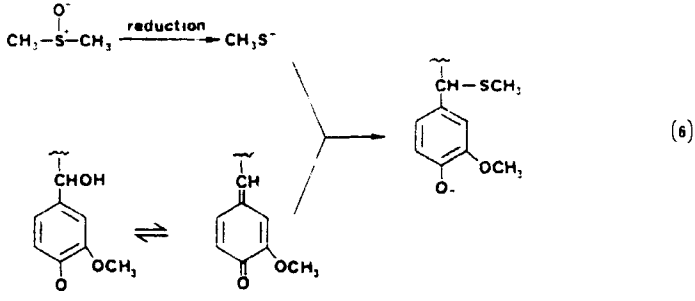
The reasons why one model gave sulfide products and the other did not are not clear. Additional studies appeared appropriate. Therefore, p-hydroxybenzyl alcohol **20** and syringyl alcohol **23** were subjected to aqueous DMSO/alkali cooks. The results are given in Eq. (4) and (5). The sulfide product **26** was identified by comparison with an authentic sample synthesized using a procedure analogous to that given by Eq. (3). Authentic samples of the

nonsulfur compounds were available for direct comparison. Condensation products 22 and 27 were expected.[23]

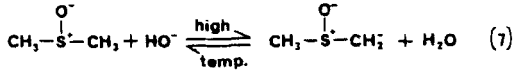




The reactions outlined above were done with commercial DMSO. Repetition of two of the cooks with freshly purified DMSO gave identical results. Thus, the methyl sulfide products do not arise from a contaminant (CH_3SH) in the DMSO. Apparently, methyl sulfide ion is generated by a reduction of DMSO during the reaction and thus adds to the quinone-methide intermediates present in the mixture to give the observed sulfide products [Eq. (6)].

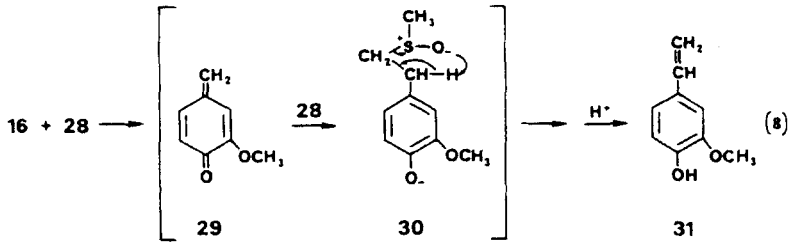


Acid/base reactions of DMSO and hydroxide ion, which give rise to dimsyl anions **28**, may be prominent at 150°C [Eq. (7)]. The basicity of hydroxide increases dramatically with temperature.[24] Dimsyl anion might react with the models and lignin, probably via quinonemethide intermediates,[5] to produce fragmentation and delignification. Quinonemethides can be generated under mild conditions by the hydrolysis of *p*-acetoxybenzylchlorides, such as **16** and **17**.[25] A few reactions of DMSO and dimsyl anions with quinonemethides generated from chloroacetates were investigated.



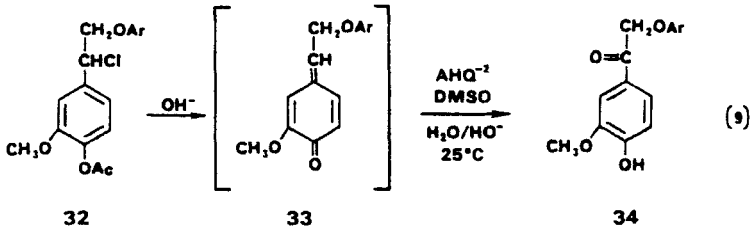
28

A DMSO solution of dimsyl anions, produced from DMSO and NaH, was mixed with chloroacetate **16** at room temperature. The major product detected by GC/MS was 4-vinylguaiacol (**31**). The presumed course of reactions giving rise to this product is shown in Eq. (8). Chemistry analogous to **30** —> **31** is known.[26]



29 **30** **31**

The degradation of chloroacetate **32** with anthrahydroquinone in alkaline 75% DMSO-water at 25° produced an interesting by-product, ketone **34** (Eq. 9). The level of ketone produced varied inversely with the level of NaOH used. None was observed when dioxane was substituted for DMSO. The production of a ketone by DMSO is not surprising, since DMSO/amines in organic solvents function as oxidizing agents.[27]



32 33 34 (9)

Dimethylsulfone ($CH_3SO_2CH_3$) is a close relative of DMSO and may be expected to exhibit some of the characteristics of DMSO. Yet, wood pulping and model cooks with dimethylsulfone showed no enhanced delignification rates or β-aryl ether cleavage. No sulfide products were observed in model cooks. Any mechanistic projections will have to reconcile these vast behavior differences with just a small change in the oxidation state of the sulfur.

CONCLUSIONS

Alkaline solutions of dimethyl sulfoxide accelerate the cleavage of β-aryl ether bonds in lignin model compounds and the dissolution of lignin from wood during pulping. Its exact mechanism of action is unclear from the experiments performed here with selected model compounds. However, the DMSO/alkali system produces several oxidation and reduction products of the models and of DMSO. The observed methyl sulfide addition products indicate that some DMSO is converted to CH_3S^- during the high temperature reaction.

Part of DMSO's "delignification effect" might be attributable to the generated CH_3S^-, which is a known pulping aid.[28] Under pulping conditions, some dimsyl anions are probably generated; these anions can add to intermediate quinonemethides and possibly facilitate cleavage of neighboring interlinkage lignin bonds. Electron transfer reactions may be important to efficient delignification,[29] and DMSO, a frequently used solvent for electron transfer reactions,[30] may facilitate such reactions.

EXPERIMENTAL

The mass spectra were obtained with a Hewlett-Packard Model 5985 GC-MS spectrometer equipped with a 2' column packed with 3% OV-1 on Chrom WHP (100-120 mesh). The GC employed a helium flow of 30 mL/min and a temperature program as follows (unless stated otherwise): hold at 120° for 3 min, raise at 25°/min to a final temperature of 285°C.

A JEOL FX 100 spectrometer was used to obtain NMR data. The pulping experiments were done with loblolly pine chips in 500 mL bombs rotated in an oil bath,[31] using the conditions given in Tables 1 and 2.

Standard Procedure. - Low temperature reactions were done in small round-bottomed flasks under a nitrogen atmosphere and agitation with a magnetic stirring bar. High temperature reactions were done in 5.5 mL capacity stainless steel bombs; the reactants were placed in the bomb, flushed with nitrogen, sealed, and immersed in a thermostatically controlled oil bath set at 153°C for 1 hr. Reactions were worked-up by cooling, neutralizing with 3M HCl, and extracting (2-3 times) with small amounts of $CHCl_3$; the combined chloroform solutions were washed several times with water, dried (Na_2SO_4), filtered, and analyzed by GC-MS.

Guaiacol-3,5-d_2. - A solution of 10 g of guaiacol in 50 g of 100% D_3PO_4 was stirred for several days in a nitrogen atmosphere. [All glassware was oven-dried before use.] The solution was extracted three times with comparable volumes of 50/50 ether-benzene. Emulsions and solubility problems cause the loss of roughly half of the organic solvent mixture. Much of the deuterated guaiacol should be in the organic phase; however, the following additional steps were taken to remove the rest of the guaiacol. The D_3PO_4 phase was dripped slowly into an excess of stirred aqueous $NaHCO_3$, and the resulting solution was extracted with 50/50 ether-benzene. The latter was washed with aqueous $NaHCO_3$ and then water, dried (Na_2SO_4), combined with the first ether-benzene extracts, and gently distilled to give 6.8 g of

partially deuterated guaiacol. Without further purification the guaiacol was treated again with 50 g of D_3PO_4 for several days and worked up as described above to give roughly 5 g of extensively deuterated guaiacol. Both NMR and GC-MS indicated that the ring protons were nearly completely replaced with deuteriums.

The crude deuterated guaiacol was placed in a titanium bomb with 15 mL of 4N NaOH, flushed with nitrogen gas, sealed, and heated at 153°C for 2 hours. The bomb was cooled, opened, and the contents were neutralized with aqueous HCl. The resulting solution was extracted several times with 50/50 benzene-ether. The combined organic extracts were dried (Na_2SO_4) and distilled to give 3 g of guaiacol-3,5-d_2, b.p. 200-210°; ^{1}H-NMR ($CDCl_3$) δ 3.85 (s, OCH_3), 5.66 (s, OH) and 6.84, 6.92 (singlets, C_4 and C_6 protons) [nondeuterated guaiacol shows a multiplet in the 6.8-7.0 region]; ^{13}C-NMR ($CDCl_3$) PPM 55.8 (s, OCH_3), 114.4 (d, C_6), 119.9 (d, C_4), 145.6 and 146.5 (singlets, C_1 and C_2), signals for C_3 and C_5 were absent; MS m/e 126 (guaiacol-d_2, 100%) and 124 (guaiacol, 1.4%).

Degradations of 1-(4'-Hydroxy-3'-methoxyphenyl)-2-(2"-methoxyphenoxy)-1-propanol (1) for Guaiacol Yields. - Stock solutions containing 10.0 mg of model 1[32] and 4.1 mg (1 equiv.) of guaiacol-3,5-d_2 per mL of either DMSO or dioxane were prepared. Another stock solution of NaOH in water (0.0484 g/mL) was also prepared. Reactions involving AHQ employed 29 mg (3 equiv. based on 1) of anthrahydroquinone diacetate and an extra 12 equivalents of NaOH. The diacetate is hydrolyzed rapidly by the base in the early stages of the reactions: AHQ-diacetate + 4NaOH ⟶ Na_2AHQ + 2NaOAc.

The reactions were performed in small stainless steel bombs of 5.5 mL capacity. Except for the pure water experiments, the bombs were charged with AHQ-diacetate (where necessary), 1 mL of solution (depending on whether AHQ diacetate was present) to give 23 equivalents of NaOH (after AHQ diacetate hydrolysis), and varying levels of water and pure organic solvent to obtain 4 mL of the desired solvent mixture. The bombs were flushed with N_2, sealed and immersed in a 153°C thermostatically regulated oil bath for 1 hour. After cooling, the bombs were opened and the contents were

acidified and stirred in air until the AHQ^{-2} (red colored) had oxidized to colorless AQ. The solids were filtered and washed with a small amount of organic solvent (DMSO or dioxane). The water diluted filtrate was extracted with 2 mL of $CHCl_3$.

A sample, 1 μL, of the $CHCl_3$ solution was analyzed by GC-MS at a column temperature of 110°C isothermal. Both guaiacol and guaiacol-d_2 eluted at 2.0 minutes. Only masses 124 and 126 were monitored and the ratio of the two ions determined. The observed ratio was compared to ratios obtained with standard guaiacol/guaiacol-d_2 mixtures to determine the yield of guaiacol produced in the reaction. Only one 2-mL $CHCl_3$ extract was analyzed, since additional extracts gave the same guaiacol/guaiacol-d_2 ratios.

For pure water degradation runs, both the model 1 and AHQ-diacetate were weighed into the bomb; guaiacol-d_2 was dissolved in dilute NaOH and pipetted into the bomb. Again, the quantities of reagents were adjusted so that the 4 mL bomb solutions contained 1 equiv. of model and guaiacol-d_2, 3 or zero equiv. of AHQ-diacetate, and either 23 or 35 equivalents of NaOH.

Each degradation was done in an identical way, and in duplicate, to give the results shown in Fig. 1.

Product Analysis of the degradation of 1-(4'-Hydroxy-3'-methoxyphenyl)-2-(2"-methoxyphenoxy)-1-propanol (1). - The standard procedure described above was employed for a 1 hr, 153° degradation of 10 mg of model 1[32] with 100 mg of NaOH in 3 mL of 50/50 DMSO-water. The GC-MS analysis showed starting material (1), guaiacol (5), and isoeugenol (6) as major components of the product mixture. Their presence was confirmed by comparing GC retention times and mass spectra with authentic samples. Several minor components were also present. One, with a retention time a little longer than isoeugenol, was assigned structure 7, 1-(4'-hydroxy-3'-methoxyphenyl)-2-propanone, based on a molecular ion at m/e 180 (20%) and a base peak at m/e 137, which could be the benzyl ion from C_1-C_2 bond cleavage; the spectrum matched that reported by Fullerton.[33] A small component preceding model 1 in the GC displayed a m/e 286 ion which would correspond to the molecular weight of vinyl ether 8.

Degradation of 1-(4'-Hydroxy-3'-methoxyphenyl)-2-(2"-methoxyphenoxy)ethanol (2). - The standard procedure was employed for a 2 hr, 153°C degradation of 0.10 g of model 2^{32} with 0.32 g of NaOH in 3 mL of water and 0.15 mL of DMSO. The three major product components, identified by comparison to authentic samples, were guaiacol (2.0 min), vinyl ether 12 (8.4 min), and 2 (8.6 min). Minor components consisted of: acetoguaiacone (9) (4.1 min), m/e 166 (45%, M^+), 151 (100%, $ArCH_2^+$) and 123 (25%, Ar^+); methyl 4-hydroxy-3-methoxybenzyl sulfide (10) (5.0 min), m/e 184 (45% M^+) and 137 (100% $ArCH_2^+$); methyl 4-hydroxy-3-methoxy-α-methylbenzyl sulfide (11) (5.1 min), m/e 198 (13%, M^+) and 151 (100%, $Ar\overset{+}{C}HCH_3$).

A corresponding degradation using 0.168 g of dimethylsulfone, 0.100 g of model 2 and 0.321 g of NaOH in 3 mL of water gave a product mixture containing model 2, vinyl ether 12, and guaiacol. Even with selected ion monitoring (SIM), products analogous to sulfides 10 and 11 were not detected. The same set of products in roughly the same ratios were observed when model 2 was degraded in the absence of either dimethylsulfone or DMSO.

Methyl 4-Hydroxy-3-methoxybenzyl Sulfide (10). - In a RB flask fitted with a condenser, magnetic stirring bar, nitrogen inlet/outlet, dropping funnel and two traps (one aq. $KMnO_4$ and the other sat. aq. $Pb(OAc)_2$ to capture CH_3SH), was added 25 mL of water, and 1.3 g (1 equiv.) of 2-methyl-2-thiopseudourea sulfate. A solution of 0.56 g of NaOH in 20 mL of water was slowly dripped into the stirred, 60°C solution to generate CH_3SNa. After stirring an additional 15 min at 60°, the solution was cooled to room temperature and 1 g of 4-acetoxy-3-methoxybenzyl chloride (16)[25] in 20 mL of dioxane was added dropwise. After stirring for 90 min, the solution was acidified and extracted with $CHCl_3$. Analysis of the $CHCl_3$ extract showed only two signals; one corresponded to 16 and the other to methyl 4-acetoxy-3-methoxybenzyl sulfide (18): MS m/e 214 (3% M^+), 184 (4%, M-ketene) and 137 (100%, $ArCH_2^+$-ketene).

A portion of the $CHCl_3$ solution of the odorous 16 was evaporated and taken up in CH_3OH. The methanol solution was stirred

at 60°C with 15 mL of 1N NaOH for 90 min, cooled, acidified and extracted with $CHCl_3$. Analysis of the $CHCl_3$ extract by GC-MS showed two principal components in nearly equal amounts; one corresponded exactly in GC retention time and MS to sulfide 10 observed in the previous reaction. The other appeared to be methyl 4-hydroxy-3-methoxybenzyl ether: m/e 168 (38%, M^+), 167 (12%, M-1), 137 (100%, $ArCH_2^+$) and 122 (21%).

Methyl 4-Hydroxy-3-methoxy-α-methylbenzyl Sulfide (11). - A procedure similar to that described above was employed to treat 0.314 g of 4-acetoxy-3-methyl-α-methylbenzyl chloride (17)[25] with 6 equiv. of *in situ* generated CH_3SNa. The workup of the reaction afforded the desired product directly, i.e., no hydrolysis was needed. The major component of the odorous product mixture corresponded exactly in GC retention time and MS to the sulfide (11) observed in the degradation of model 2. Two minor low retention compounds were also observed: 31, MS m/e 150 (100%, M^+), 135 (96%, M-15), 107 (41%) and 77 (54%) and α-methyl-4-hydroxy-3-methoxybenzyl alcohol, MS m/e 168 (50%, M^+), 153 (78%, M-15) and 93 (100%).

Methyl 4-Hydroxy-3,5-dimethoxybenzyl Sulfide (26). - A procedure identical to that described above was employed using 30 mg of 4-acetoxy-3,5-dimethoxybenzyl chloride. The latter was prepared by treating syringyl alcohol with acetylchloride:[25], ^{1}H-NMR δ ($CDCl_3$) 2.32 (s, 3, Ac), 3.82 (s, 6, OCH_3), 4.54 (s, 2, $-CH_2Cl$) and 6.63 (s, 2, aryl); IR (mull) 1760 cm^{-1} (ester C=O). Analysis of the sulfide addition product mixture showed starting chloroacetate, MS m/e 202/204 (35%, M^+) and 167 (100%, $ArCH_2^+$) and sulfide 26, MS m/e 214 (19%, M^+), 167 (100%, $ArCH_2^+$) and 123 (14%).

Degradation of p-Hydroxybenzyl Alcohol (18). - The standard procedure was employed for a 1 hr, 153°C degradation of 0.1 g of 20 with 0.1 g of NaOH in 3 mL of 50/50 DMSO-water. Analysis of GC-MS showed only two main components: the low retention time component was methyl-p-hydroxybenzyl sulfide (21), MS m/e 154 (21%, M^+), 107 (100%, $ArCH_2^+$) and 77 (18%); the high retention time peak

was bis-(p-hydroxyphenyl)methane (22), MS m/e 200 (74%, M^+), 199 (31%, M-1) and 107 (100% $ArCH_2^+$).[34]

Degradation of Syringyl Alcohol (23). - The standard procedure was employed for a 1 hr, 153°C degradation of 0.1 g of syringyl alcohol (21) with 0.1 g of NaOH in 3 mL of 50/50 DMSO-water. Analysis by GC-MS showed an abundant component at 9.8 min which corresponded to the dimer 27,[35] MS m/e 320 (100%, M^+), 289 (50%, $M-CH_3O$) and 167 (75%, $ArCH_2^+$), a moderate component (6.5 min) corresponding to sulfide 26, which had an identical retention time and MS to the material prepared above, and minor components at 3.7 min and 5.5 min corresponding to 2,6-dimethoxy-4-methyl phenol (24),[14] MS m/e 168 (100%, M^+) and 153 (61%, $M-CH_3$), and syringaldehyde (25),[35] MS m/e 182 (100%, M^+) and 181 (65%, M-H).

A degradation of syringyl alcohol without DMSO or with dimethylsulfone gives the same product mixture except no sulfide 26 was observed.

Dimsyl Anion Reaction with Chloroacetate (16). - A mixture of 2.0 g (83 mmoles) of sodium hydride in 50 mL of freshly distilled DMSO (in dry glassware, under a nitrogen atmosphere) was stirred for 2 1/2 hr at 75°C, cooled to room temperature, and then 2.0 g (9 mmoles) of 4-acetoxy-3-methoxybenzyl chloride (16)[25] dissolved in 10 mL of DMSO was added dropwise. After stirring overnight, the solution was poured into an excess of water, acidified with 3N HCl, and extracted with $CHCl_3$. The combined $CHCl_3$ extracts were washed with water, dried (Na_2SO_4), and evaporated. Analysis of the resulting residue showed only a single component, 4-vinylguaiacol (31), identical to an authentic sample, MS m/e 150 (100%, M^+), 135 (75%, $M-CH_3$), 107 (20%), and 77 (22%).

A similar reaction done with dimethylsulfone gave starting material (16) at 5.0 min in large amounts, 1,2-di(4-hydroxy-3-methoxyphenyl)ethane,[34] MS m/e 274 (12%, M^+) and 137 (100% $ArCH_2^+$), at 8.5 min in small-moderate amounts, and several minor components in the 8-11 min region.

Degradation of 1-Chloro-1-(4'-hydroxy-3'-methoxyphenyl)-2-(2'methoxyphenoxyl)ethane (32). - A mixture of 302 mg (3

equiv.) of AHQ-diacetate in 40 mL of 75% DMSO-water, containing 301 mg (22 equiv.) of NaOH and 48.5 mg (1 equiv.) of cresol (internal standard), was stirred for 15 min at 25°C and then 120 mg (1 equiv.) of solid chloroacetate 32^{32} was added. Samples were withdrawn at various time intervals, worked-up in the standard manner and analyzed by GC-MS. Each sample contained β(o-methoxyphenoxy)-4-hydroxy-3-methoxyacetophenone (34). The level of 34 increased (relative to the creosol) with time.

Similar runs were done with higher and lower NaOH concentrations. The observed level of ketone 34 decreased with increasing base concentration. No ketone 34 was observed when dioxane was substituted for DMSO.

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