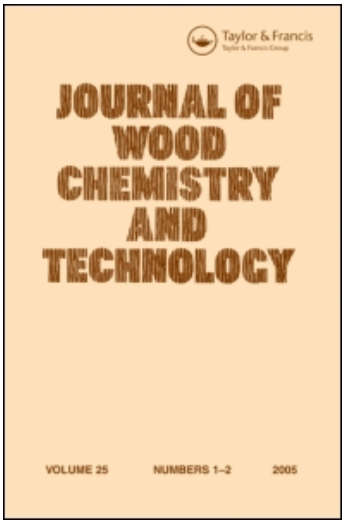

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Structural/Reactivity Studies (I): Soda Reactions of Lignin Model Compounds

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STRUCTURAL/REACTIVITY STUDIES (I): SODA REACTIONS OF LIGNIN MODEL COMPOUNDS

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ABSTRACT

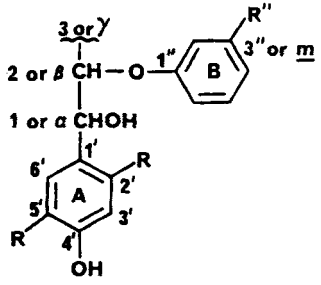
Lignin model compounds containing a phenolic "A" ring, α-OH, and β-aryl (ring "B") ether, with different substituents located on rings A and B, have been synthesized and degraded under a variety of conditions in sodium hydroxide-water (soda). Substituent changes on ring B had a large effect on fragmentation reactions of the models; changes on ring A showed only small effects. These substituent-reactivity relationships indicate that the slow step in the mechanism for model fragmentation under soda conditions is cleavage of the β-aryl ether bond. Vinyl ether formation, a reaction which competes with model fragmentation, is more prominent at low alkali concentration.

INTRODUCTION

Structure-reactivity studies consist of examining the rates of reaction of several closely related compounds and correlating the rate data with differences in structure in order to provide information on reaction mechanisms. We have synthesized and examined the rates of degradation of several related lignin model compounds. Our initial goal was to demonstrate the importance of electron transfer reaction mechanisms in pulping systems.[1,2] This report (soda reactions) and the one which follows (soda-additive reactions) describe our results with a structure-reactivity study of delignification mechanisms.

0277-3813/86/0604-0535$3.50/0

Two model series (1 and 2) were studied. Their definition and numbering system are given below. The term "fragmentation" refers to cleavage of the β-aryl ether bond. Substituents meta on ring B were chosen to minimize steric effects and ambiguous resonance effects. Should the B ring break off as a phenolate radical, all groups ortho and para can stabilize by resonance; the principal effect at the meta position is a simple polar effect.[3] Substituents located on the B ring would be expected to have a significant effect on reaction rates if cleavage of the β-aryl ether bond were the rate determining step in the mechanism. Substituents on the A ring would be expected to have little effect on the rate if the cleavage step were the slow step.



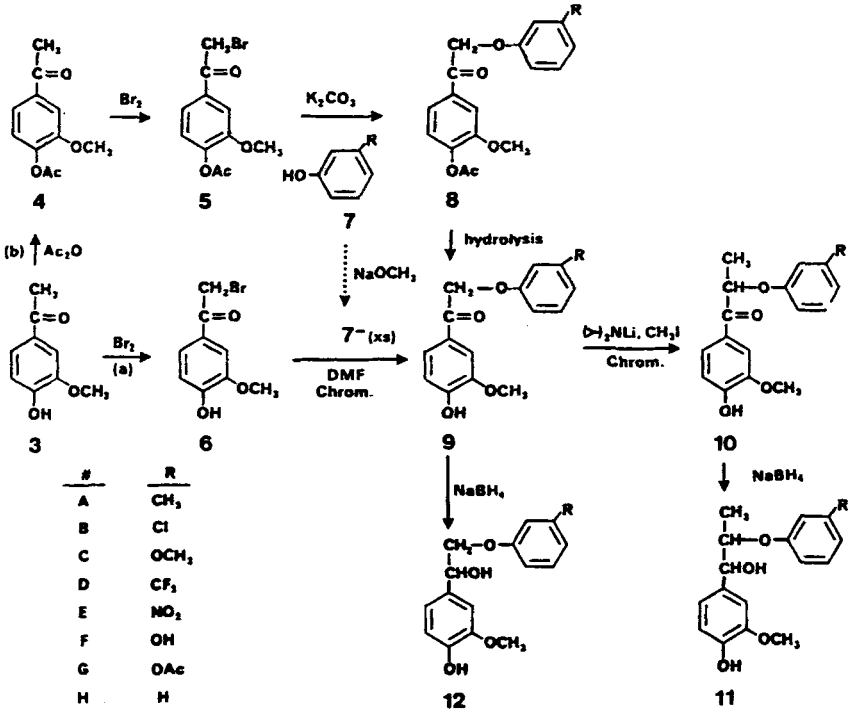
1, vary R'' (ring B), R=OCH_3, R'=H
2, vary R and R' (ring A), R''=CH_3 or CF_3

Synthesis

The synthetic steps used to prepare the m-substituted ring B models are given in Scheme 1 and are analogous to those steps previously used to prepare model 13.[4] The shorter pathway to ketone 9 (path a) was the method most often used. The longer pathway b allows purification of each intermediate and does not require an excess of phenol in the coupling step. In several cases, however, problems arose during the coupling step; a portion of the acyl groups transferred from 5 to 7 during the reaction, resulting in low yields and mixtures, and requiring chromatographic isolations.

SCHEME 1

Steps in the Model Syntheses

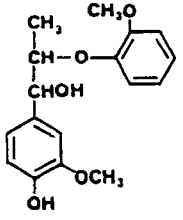


Direct reduction of ketones 9A-F gave the non-β-methyl (or C_2) series of alcohols (12A-F). Methylation of 9A-D and their reduction gave the β-methyl (or C_3) series of alcohols (11A-D). The m-OH and m-NO_2 C_3-models (11F and E) were not prepared because of both synthetic difficulties and reactivity problems. Preliminary degradations of C_2-alcohols 12F and E indicated that these two model types would not be of general use for all the anticipated experiments. The nitro group was readily reduced by anthrahydroquinone (AHQ), and phenol model (12E) gave undesirable by-products when degraded in alkali. The abandonment of the m-NO_2 and m-OH series left us without our most and least reactive models.

Why two sets of B-ring analogs? Our interest was initially only in C_3-models, 11, even though their synthesis and characterization presents more problems than the C_2-models, 12. Previous studies with 13 and 14 demonstrated the value of using the larger model.[5] Quantification of the B-ring phenol (guaiacol) from degradations done in the presence of AHQ was difficult for the C_2-analog, 14. The guaiacol recovery problem is, however, probably only limited to AHQ reactions. Soda model reactions should give little, if any, 4-vinylguaiacol,[6] a styrene by-product which has adverse affects on the quantification of guaiacol. Indeed, the C_2-m-R B-ring substituted models (12) behaved well in the soda degradations; phenol yields were reasonable and reproducible.

Two analogs of the C_2-m-methyl alcohol 12A, having different ring A substituents, were also synthesized. Model 23 was made by brominating commercially available ketone 16 to give 18, coupling this product with m-cresol to give 20, and reducing the latter with $NaBH_4$. The synthesis of model 24 began with a Fries rearrangement of 15 to 17, followed by bromination to 19, coupling with m-cresol to ketone dimer 21, and finally $NaBH_4$ reduction. A similar sequence was used to prepare 25, a m-CF_3 analog.

Models differing in substituents on the A ring would be expected to provide less information than B ring models concerning the mechanism of soda promoted fragmentation. They were, however, studied to verify the B ring model soda results and provide valuable information in the additive experiments (accompanying paper).



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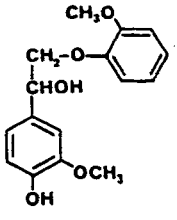

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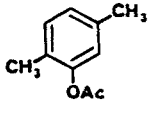

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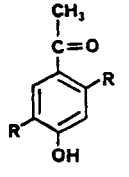
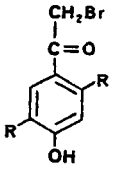


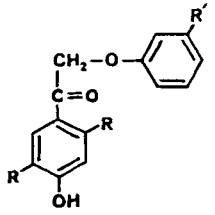
16, R = H

17, R = CH_3



18. R = H

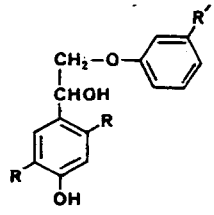
19. R = CH_3



20. R = H, R′ = CH_3

21. R = R′ = CH_3

22. R = CH_3, R′ = CF_3



23. R = H, R′ = CH_3

24. R = R′ = CH_3

25. R = CH_3, R′ = CF_3

Phenol Analysis

A reliable analytical procedure was needed to determine the extent of fragmentation of the model compounds under varying conditions. Analysis of changes in the level of starting material (model compound) with time has many problems associated with it. For example, the model can be lost *via* reactions, such as vinyl ether formation, which are not fragmentation reactions of the β-linkage. Also, the α-hydroxy models dehydrate easily upon gas chromatography (GC) analysis. The simplest indicators of fragmentation of the model are the B ring phenols produced.

In general, the level of ring B phenol produced is taken to be indicative of the extent of fragmentation (or delignification).[6] In our case, some of the ring B phenols are reasonably water soluble - making quantification difficult when extraction steps are involved. We therefore developed two analytical methods which convert an alkaline phenol solution into water insoluble phenol derivatives; each involved GC analysis and the use of *p*-isopropyl phenol as an internal standard (IS).

The one method consisted of methylation of the phenols with dimethylsulfate. The other method, benzoylation in the presence of a phase transfer catalyst, was the most reproducible but was only successful with selected phenols. The agreement between methods was good, where appropriate.

Model Degradations - General

The lignin model compounds were dissolved in deoxygenated water containing NaOH and placed in small pressure vessels along with any additional water or water-NaOH solutions. All operations were done in a glove bag under a nitrogen atmosphere. The pressure vessels were sealed under nitrogen, rotated in a prewarmed oil bath for specific time periods, cooled, opened, and emptied. The reacted solutions were diluted with a known level of IS, dissolved in aq. alkali, derivatized by methylation or benzoylation, and analyzed by GC.

Product mixtures, both before and after derivatizations, were also examined by GC-mass spectroscopy (MS). The only volatile products observed were starting materials (α-hydroxy models), vinyl ethers, the ring B phenols, and guaiacol. The latter, which is present only in small amounts, must arise from ring A by cleavage of the C_α-ring carbon bond.

RESULTS

Model Degradations - Ring B Analogs

Models 12A-D (m-R, B ring analogs) were placed in the same reaction vessel and heated at 170°C with high levels of NaOH to produce the data shown in Fig. 1. There are three aspects of this data which need discussing: (1) the change in fragmentation rate at about 20 min, (2) the change in fragmentation efficiency with the level of NaOH used, and (3) the change in the degree of fragmentation as the B ring substituent was varied.

The change in fragmentation rates at 20 min is probably associated with a secondary fragmentation process. Analysis by GC-MS showed essentially no starting materials were left after 40 min for both the high and low NaOH level degradations; only simple ring B phenol and cis/trans isomers of vinyl ethers remained (Fig. 2). Vinyl ether by-products have also been observed in the soda induced degradation of the guaiacyl B ring model 14.[7,8]

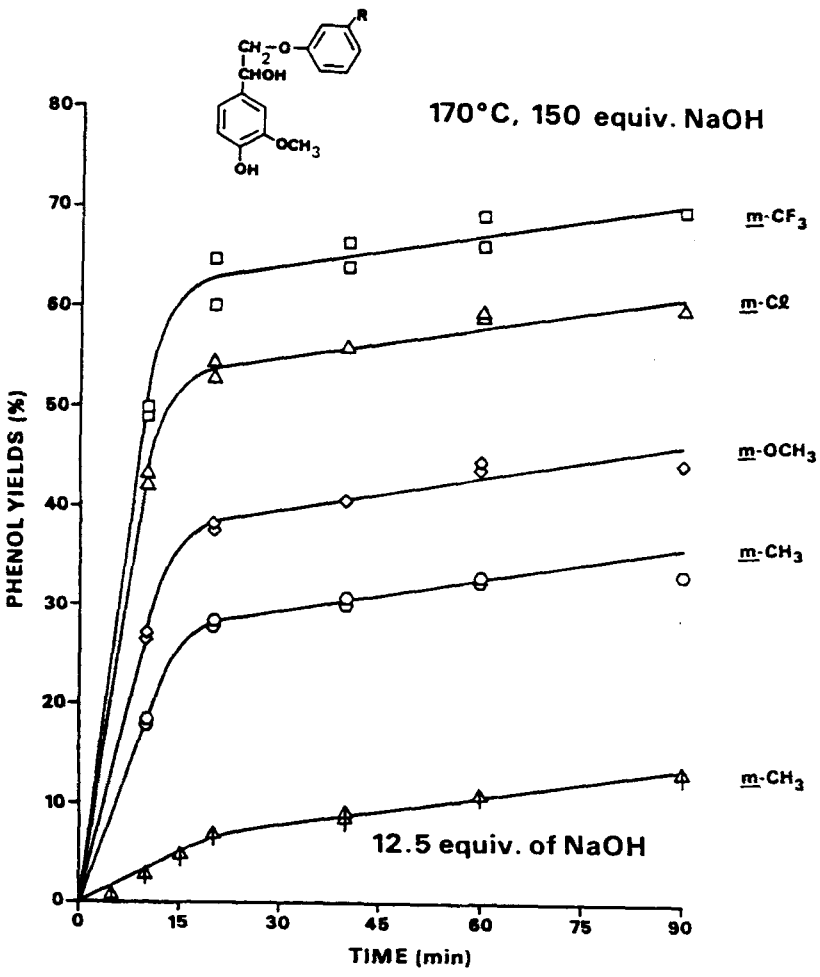


Figure 1. Phenol yields as a function of time in the simultaneous degradation of models 12A–D at 170° in the presence of 150 equivalents of NaOH (upper four curves) and the single degradation of 12A at 170° with 12.5 equiv. of NaOH (lower curve).

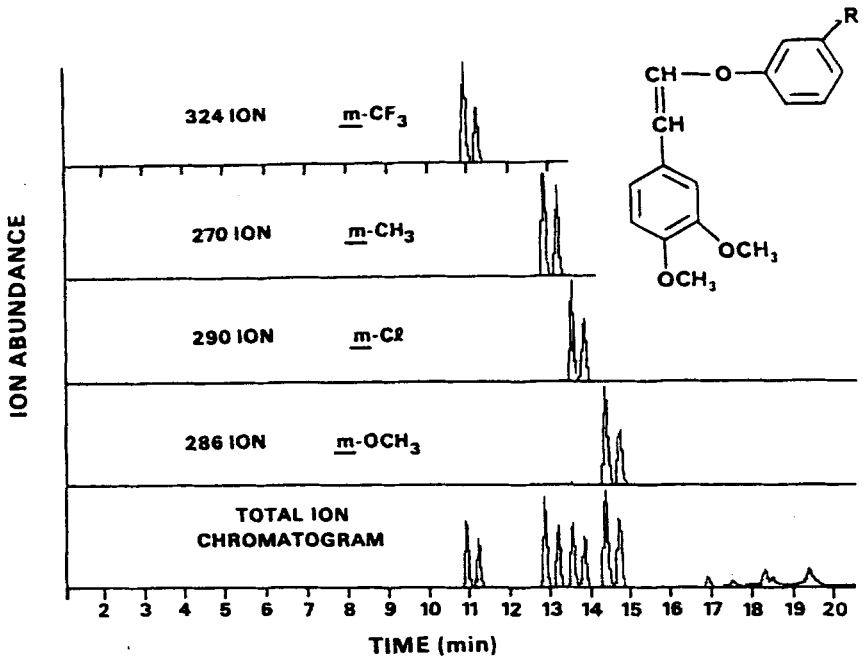
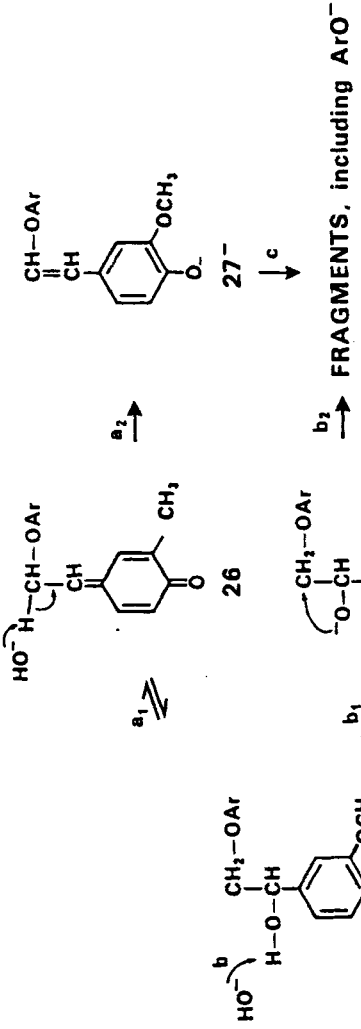


Figure 2. GC-MS analysis of the 40 minute methylated product mixture from the simultaneous degradation of models 12A-D at 170° with 150 equiv. of NaOH. Ion selection (top portion of the figure) shows the various cis/trans vinyl ethers (27) derived from 12A-D. The bottom portion of the figure displays the total ion chromatograph. Early signals due to phenol fragments are not present because of a time delay which was used in the analysis; the later signals correspond to dimers of vinyl guaiacol.

A cis/trans mixture of vinyl ethers derived from the m-methyl model 12A (specifically, 27, R=CH_3, Fig. 2) was synthesized, characterized, and degraded in alkali at 170°C. The rate of fragmentation of the synthesized vinyl ether mixture was similar to the slow fragmentation rate observed for model 12A and was unaffected by the level of NaOH used over a range of 25-150 equiv./model.

SCHEME 2

Modes of Soda Induced Decomposition of Models 12



The observed data best fit the reaction sequences shown in Scheme 2. In the first few minutes of alkali treatment, the α-OH models are apparently converted both to vinyl ethers (path a) and directly fragmented (path b). After 20 min of treatment, all that remain are fragmented products and vinyl ethers; the latter slowly fragment thereafter (via undefined path c or a reversal of path a).

Vinyl ether fragmentation rates appear to be insensitive to B ring substituents, since the model fragmentation rates are the same after 20 min (Fig. 1). This observation helps to define the nature of the slow step in the vinyl ether fragmentation mechanism; for example, quinonemethide generation, the reverse of step a_2, could be the slow step.

The B ring phenol yield is strongly dependent on the level of NaOH used in the degradation of the α-OH models. This fact has been demonstrated by reaction time vs. phenol fragment yield studies (Fig. 1) and by observing phenol yields at specific times when employing different levels of NaOH. The phenol yields did not vary much when the ratio of NaOH/model were 5-25/1, but showed significant increases at the 80/1 and 150/1 ratios. Holding the ionic strength constant by the addition of NaCl had little effect.

Acceleration of fragmentation of β-aryl ether models by increasing the alkali strength has also been observed by others.[7,9] It appears that the rate of vinyl ether generation is fast and is dominant at low NaOH levels. At high NaOH levels a shift in the $12^{-} + HO^{-} \rightleftharpoons 12^{-2} + H_2O$ equilibrium toward 12^{-2} probably occurs. According to Scheme 2, increasing the level of 12^{-2} in the system should favor fragmentation.

The initial rate of fragmentation and also the final extent of fragmentation followed the order m-CF_3 > m-Cl > m-OCH_3 > m-CH_3 for the C_2-models of the type 12. This same order was observed at 135°C and 150°C for 12A-D and for the C_3-models 11A-D at 150°C; the magnitude of the differences was, however, much less at the lower temperatures. The order of reactivity indicates that electron withdrawing groups aid the direct fragmentation of the models. In

fact there is a good correlation between the model reactivities and the substituents' Hammett sigma values (Table 1, Fig. 3).

An electron withdrawing group on ring B would be expected to favor either step (b_1 or b_2) in the proposed direct fragmentation mechanism (Scheme 2). A group such as CF_3 would favor step b_1 (base abstraction) by increasing the acidity of the α-OH proton and step b_2 (β-aryl ether cleavage) by stabilizing the ring B phenolate ion fragment.[3] The fact that the ρ-value (the slope of the 10-minute line in Fig. 3) is roughly + 0.7 indicates that the cleavage step is probably the rate determining step in the sequence.

The ρ-value is a measure of the sensitivity of the reaction to ring substitution.[3] Reactions performed at elevated temperatures should be influenced less by substituent changes than those done at room temperature. Consequently, the magnitude of a ρ-value should decrease with increasing temperature. Based on the temperatures employed (170°C) in the degradations and the large distance between the meta ring substituents and the α-OH group, one would expect that the ρ-value for step b_1 of the mechanism would be less than + 0.2.[3] The observed value of + 0.7 is more in accord with the generation of the B-ring phenolate ion as the slow step, since the expected ρ-value would be about + 1.0 to 2.2 at room temperature.[3]

Besides temperature effects, the magnitude of the differences (a reflection of the ρ-value) between the substituents CF_3, Cl, OCH_3, and CH_3 could be attenuated by competing vinyl ether formation reactions. There is evidence from another study[9] that a_2 (C_β-proton abstraction) is the slow step in the sequence of reactions leading to vinyl ether products. Therefore, models with electron withdrawing groups on ring B should give rise to more vinyl ether products than models with electron releasing groups on ring B. When the rate of vinyl ether formation increases, there will be less direct model fragmentation. Thus, a CF_3 group should promote both rapid direct model fragmentation and rapid vinyl

TABLE 1

Hammett σ Values[a,3]

Substituent	σ_m
NO_2	+ 0.71
CF_3	+ 0.42
Cl	+ 0.37
OCH_3	+ 0.12
CH_3	- 0.17
O^-	- 0.71

[a]Groups which supply electrons have negative (-) σ values; groups which withdraw electrons have positive (+) σ values. The magnitude of the σ values reflects how well they supply or withdraw electrons.

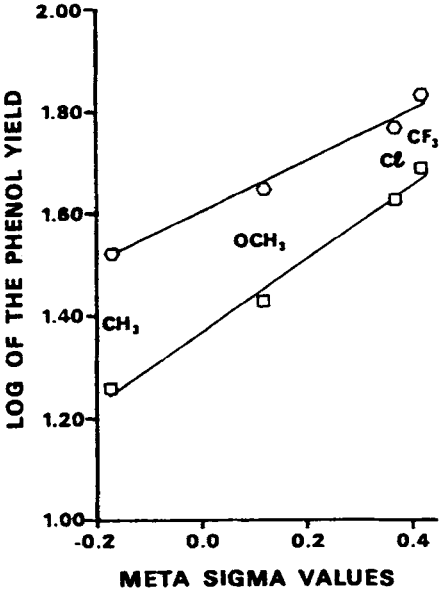


Figure 3. Correlation of σ_m values with the log of the phenol liberation yields obtained from Fig. 3: □ , 10 min yields; ⬡, 60 min yields.

ether formation, with the latter reaction detracting from the overall potential yields of the former reaction.

Finally, in a direct comparison of the m-CH_3 and m-CF_3 models 24 and 25, the latter fragmented nearly twice as much as the former. Thus, the reactivity differences between the m-CH_3 and m-CF_3 models are not affected by changes in the ring A substituents.

Model Degradations - Ring A Analogs

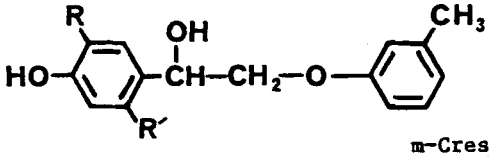
A direct comparison of the aq. alkaline degradations of ring A model analogs at 170°C produced the data shown in Table 2. The observed reactivity differences probably reflect a combination of polar and steric substituent effects. The unusually high reactivity of the dimethyl model 24 may be the result of a steric effect by the 2'-methyl group which retards vinyl ether and/or condensation side reactions; thus, fragmentation reactions take on greater prominence. Crowding effects on the β-carbon also enhance model fragmentation.[5]

Cleavage of the β-aryl ether bond (step b_2, Scheme 2) should not be influenced by substituents on ring A and, indeed, models 12A and 23 have similar reactivities. Ring A substituents may, however, affect the balance between the competing fragmentation and vinyl ether formation reactions. If vinyl ether reactions are favored, fragmentation yields will decrease and vice versa.

The observed similar reactivity of 3'-methoxy model 12A and the unsubstituted model 23 provides information on the mechanism of formation of vinyl ether products. Quinonemethide formation is greatly accelerated by a methoxyl group at the 3'-position of ring A (see accompanying article). If QM generation (step a_1, Scheme 2) is the slow step in vinyl ether formation, the substitution of a methoxy group on ring A would lead to more vinyl ether products and significantly less direct fragmentation. Yet, the m-cresol yields from 12A were slightly greater than those from 23. Consequently, the slow step in vinyl ether generation appears to

Table 2

m-Cresol Yields from Degradation of A-Ring Models[a]



Cpd.	R	R'	m-Cresol Yield, (%) 20 minutes	40 minutes
12A	OCH_3	H	5.9, 5.3	8.0, 9.0
23	H	H	4.2, 4.4	7.9, 7.4
24	CH_3	CH_3	9.9, 9.8	14.4, 12.1

[a]The conditions were 170°C in the presence of 25 equiv. of NaOH.

be C_β-proton abstraction (step a_2) and not QM generation; this conclusion supports the findings of Gierer and Ljunggren.[9]

The acidity of the C_β-proton should be affected by ring substituents and, because of direct conjugation, ring A groups should be more effective. This logic leads to the prediction that electron withdrawing groups on ring A (i.e., m-OCH_3, σ +0.12) would favor C_β-proton abstraction (and vinyl ether formation) and give poorer yields of direct fragmentation. Although the differences are small, just the opposite was found. Under the harsh conditions employed, substituent effects on C_β-H ionization may be small.

CONCLUSIONS

The level of hydroxide used in soda treatments of m-R ring B substituted models 12A-D dictates the course of degradation reactions taken, vinyl ether formation or direct fragmentation. The slow step in the direct fragmentation appears to be cleavage of the β-aryl ether bond. This conclusion is based on the observation that B ring substituents are strongly involved in the transition state of the rate determining step.

Vinyl ether by-products also fragment at their β-aryl ether linkages, but at a much slower rate than the direct fragmentation of the α-hydroxy-β-aryl ether model phenols. The rate of vinyl ether fragmentation is unaffected by substituents on ring B.

The formation of vinyl ether products appears to involve two steps, quinonemethide production and C_β-proton abstraction. The latter step appears to be the slow step.

EXPERIMENTAL SECTION

The equipment has been previously described.[10] All melting points are corrected. Most of the methods used to prepare the compounds described in this report were identical to procedures already published for very similar compounds and, therefore, will not be described here in individual detail. These methods include coupling of β-bromoketones with phenolate ions to give dimer model ketones **9A-D**, **9F**, and **20-22**;[4] methylation of dimer model ketones to give **10A-D**;[11] and sodium borohydride reduction of model ketones to give α-hydroxy models **11A-D**, **12A-F**, and **23-25**.[4]

The methylation of chloroketone **9B** produced an unusual result: a portion (roughly 40%) of the chloro groups were reduced, giving rise to a product mixture composed of C_2- and C_3-chloroketones **9B** and **10B**, along with the C_2- and C_3-unsubstituted ketones **9H** and **10H**. Separation of all four components of this mixture by column chromatography proved difficult, although a small sample of pure **10B** was obtained.

The physical data and NMR data for the compounds prepared by standard methods are given in Tables 3-7. All the compounds in these tables showed infrared signals cm^{-1} at 3200-3400 (OH) and typical aryl absorptions; compounds **9A-F**, **10A-D**, and **20-22** also showed 1660-1670 (C=O).

4-Acetoxy-3-methoxy-α-bromoacetophenone (5). A sample of 15.0 g of 4-acetoxy-3-methoxyacetophenone (4)[12] was brominated using a procedure similar to that of Erdtmann and Leopold[13] to give 9.0 g (44% yield) of colorless crystals, m.p. 85.0-87.0°C from ethanol

TABLE 3

Selected Physical Data for Synthesized Compounds

Cpd.	% Yield[a]	m.p. (°C) Solvent[b]	Mass Spectrum, m/e (%)[c]
9A	53	170.5-172.5 (aq. EtOH)	272(M^+,22), 151(100), 137(5), 123(8), 108 (4), 91 (7), 77 (4), 65 (7)
9B	82	118-9 (tol.)	292/294(M^+,12), 151(100), 137(4), 123(9), 122(3), 111(3), 108(3)
9C	75	109-10 (tol./p.e.)	288(M^+,16), 151(100), 137(6), 123(10), 108(6), 92(6), 77(9), 65(5)
9D	88	107.5-8.5 (benz./p.e.)	326(M^+,12), 151(100), 145(14), 123(13), 108(8), 77(5), 65(7)
9E	65	187.5-9.5 (EtOH)	303(M^+,5), 151(100), 123(12), 122(4), 108(5), 94(3), 77(3), 76(3), 65(4)
9F		145-6 (benz.)	274(M^+,27), 152(9), 151(100), 137(7), 123(12), 93(5), 65(9)
10A	48	86-8 (benz./p.e.)	286(M^+,18), 151(100), 135(23), 123(7), 108(4), 107(4), 91(15), 77(3), 65(7)
10B		117.5-9.5	306/308(M^+,8), 151(100), 123(10), 111(8), 108(6), 91(8), 77(6), 65(7)
10C	32	131-2 (benz./p.e.)	302(M^+,28), 151(100), 123(16) 77(19)
10D	12	121-3 (tol.)	340(M^+,10), 152(9), 151(100), 145(6), 123(8)
12A	89	94-6 (tol.)	274(M^+,12), 153(100), 137(13), 125(37), 122(40), 93(56), 91(29), 77(11), 65(38)
12B	88	132-4 (tol.)	294(M^+,6), 154(9), 153(100), 125(13), 93(30), 65(14)
12C	85	101-2.5 (tol.)	290(M^+,14), 166(15), 153(100), 138(26), 137(14), 125(19), 107(10), 93(35), 77(14), 65(15)
12D	93	125-5.5	328(M^+,17), 154(9), 153(100), 145(10), 125(15), 93(33), 65(13)

See end of table for footnotes.

12E	98	138-40	305(M^+,7), 153(100), 125(21), 110(6), 93(47), 77(9), 65(20)
12F		120-3 (benz.)	276(M^+,5), 153(100), 137(14), 125(33), 124(22), 110(17), 93(91), 81(22), 77(17), 65(70)
17[d]	49	131-2 (benz.)	164(M^+,41), 150(10), 149(100), 121(17), 91(15), 77(14), 65(6)
18[e]	23	132-3 (ether)	214/216(M^+,16), 122(8), 121(100), 107(10), 93(14), 77(5), 65(13)
19[e,f]	62	129-31 (ether)	242/244(M^+,19), 164(6), 150(10), 149(100), 135(6), 121(12), 91(14), 77(10), 65(5)
20	44	170.5-2.5 (aq. EtOH)	242(M^+,14), 122(8), 121(100), 107(5), 93(8), 91(6), 65(11)
21	54	188.5-90.5 (acetone)	270(M^+,16), 150(10), 149(100), 135(3), 121(8), 91(14), 77(10), 65(8)
22	87	191-4 (tol.)	324(M^+,2), 150(10), 149(100), 145(9), 135(3), 121(6), 91(12), 77(9), 65(3)
23	60	94.5-6 (tol.)	244(M^+,6), 136(15), 123(100), 122(45), 108(13), 95(17), 91(18), 77(18), 65(11)
24	85	100.5-3.5 (tol.)	272(M^+,8), 152(10), 151(100), 135(11), 123(21), 122(31), 108(10), 91(19), 77(12), 65(9)
25	75	145.5-7 (tol.)	326(M^+,4), 175(3), 152(10), 151(100), 145(15), 123(17), 108(7), 91(7), 77(7)

[a]All yields are of purified products, often after column chromatography and recrystallization; omitted yields were difficult to determine (i.e., materials for more than one run combined).
[b]Recrystallization solvents: benz. = benzene, tol. = toluene, p.e. = pet. ether. The lack of indicated solvent means recryst. was not performed.
[c]M = molecular ion.
[d]Known compound;[15] lit. m.p. 130-1°C.
[e]Prepared by the standard bromination procedure.[4]
[f]A 70:30 mixture, see Exp. Section.

TABLE 4

NMR Data for Ketone Models 10[a]

Cpd.	m-R	OCH_3	ArOH	C_1	C_2	C_3	Aryl Signals[b]
10A[c]	2.26	3.89	6.23		5.40	1.69	6.6-7.2(m,5) and 7.6-7.8(m,2)
	21.5	56.0		197.6	76.6	19.4	111.0, 111.8, 114.0, 116.1, 122.2, 124.2, and 129.2(d); 126.9, 139.6, 146.8, 150.9, and 157.5(s)
10B[c]		3.90	6.29		5.42	1.69	6.65-7.25(m,5) and 7.36-7.75(m,2)
		56.0		196.3	76.6	19.1	110.6, 113.0, 113.8, 115.6, 121.3, 123.8, and 130.0(d); 126.4, 134.7, 146.5, 150.8, and 157.8(s)
10C[c]	3.83	3.91	6.24		5.43	1.72	6.8-6.9(m,5) and 7.3-7.8(m,2)
	55.1	55.9		196.9	76.3	19.0	101.5, 106.8, 106.9, 110.6, 113.8, 123.8, and 129.7(d); 126.6, 146.5, 150.6, 158.4, and 160.5(s)
10D[c]		3.93	6.13		5.49	1.73	6.9-7.4(m,5) and 7.6-7.8(m,2)
	f	56.1		196.3	76.6	19.3	110.7, 112.2, 112.5, 114.0, 117.8, 123.9, and 130.0(d); 126.5, 131.8,[g] 146.8, 151.1 and 157.4(s)

[a] Signals in δ are relative to TMS zero. While splitting patterns and integration areas are not indicated here, they were in accord with the assignments, i.e., OCH_3 appeared as a singlet (rel. area 3) in the ^{1}H-NMR and a quartet in the off-resonance coupled ^{13}C-NMR. Proton signals are given first, carbon-13 signals next.

[b] Numbers and letters inside the parentheses refer to relative areas and splitting, respectively: m = multiplet, s = singlet, d = doublet.

[c] $CDCl_3$ solvent. [d] Acetone-d_6 solvent. [e] DMSO-d_6 solvent.

[f] The $\underline{C}F_3$ carbon was not observed as a separate signal; this is probably due to the slow relaxation of the carbon and the quartet splitting as a result of three ^{19}F (spin 1/2) atoms.

[g] The splitting remains the same in the coupled and decoupled spectra, a quartet (J = 1.3 ppm), $\underline{C}$-CF_3.

TABLE 5

NMR Data for Ketone Models 9[a]

Cpd.	m-R	OCH_3	ArOH	C_1	C_2	Aryl Signals[b]
9A[c]	2.30	3.92	6.33		5.19	6.7-7.2(m,5) and 7.6-7.7(m,2)
	21.5	56.1		193.1	70.6	110.1, 111.5, 114.0, 115.6, 122.4, 123.4, and 129.2(d); 127.4, 139.6, 146.8, 151.0, and 158.0(s)
9B[c,d]		3.95	6.20		5.22	6.8-7.0(m,5) and 7.5-7.6(m,2)
		56.2		192.1	70.8	111.3, 114.1, 115.3, 115.5, 121.4, 123.5, and 131.0(d); 127.6, 134.8, 148.1, 152.5, and 160.0(s)
9C[c]	3.78	3.95	6.12		5.20	6.4-7.2(m,5) and 7.5-7.6(m,2)
	55.4	56.2		192.6	70.5	101.5, 106.6, 107.2, 110.1, 114.0, 123.3, and 129.8(d); 127.4, 146.8, 150.9, 159.1, and 160.7(s)
9D[c,d]		3.96	6.20		5.28	6.9-7.4(m,5) and 7.5-7.6(m,2)
	f	56.2		192.0	70.8	111.2, 112.2, 115.3, 118.0, 119.1, 123.6, and 130.8(d); 127.6, 131.8,[g] 148.1, 152.6 and 159.4(s)
9E[c]		3.96	6.06		5.28	6.9-7.0(d,1), 7.2-7.6(m,4) and 7.7-7.9(m,2)
		55.7		191.5	70.2	108.9, 111.0, 115.1, 115.6, 121.9, 122.9, and 130.4(d); 125.8, 147.6, 148.5, 152.3, and 158.5(s)
9F[c,e]	5.08	3.95	6.13		5.20	6.13(s,1), 6.4-6.5(m,3), 6.9-7.2(m,2) and 7.5-7.6(M,2)
		55.5		192.5	69.6	101.7, 105.2, 107.9, 110.9, 114.9, 122.7, and 129.6(d); 126.0, 147.5, 152.1, 158.3, and 159.0(s)

[a-f] See Table 4 for footnotes.

TABLE 6

NMR Data for Models of Type 12[a]

Cpd.	m-R	OCH_3	ArOH	ROH	C_1	C_2	Aryl Signals[b]
12A[d]	2.32	3.90	5.65	2.80	4.99	4.03	6.7-7.2(m,7)
	21.5	56.2			72.6	74.3	110.7, 112.3, 115.2, 116.0, 119.7, 122.0 and 129.7(d); 134.1, 139.7, 146.5, 147.8 and 159.7(s)
12B[d]		3.91	7.48	4.59	4.95	4.05	6.7-7.4(m,7)
		56.1			72.4	74.6	110.6, 114.0, 115.1, 115.5, 119.6, 121.1 and 131.1(d); 133.6, 134.8, 146.5, 147.8 and 160.5(s)
12C[d]	3.78	3.91	5.64	2.75	5.04	4.02	6.5-6.6(m,3) and 6.9-7.3(m,4)
	55.4	56.2			72.5	74.4	101.5, 107.0, 107.4, 110.6, 115.2, 119.6 and 130.4(d); 133.9, 146.5, 147.8, 160.8 and 161.5(s)
12D[d]		3.92	5.66	2.69	5.07	4.08	6.9-7.5(m,7)
	f	56.2			72.5	74.8	110.7, 112.1, 115.2, 117.6, 119.1, 119.7 and 131.0(d); 131.2,[g] 133.6, 146.6, 147.9 and 160.0(s)
12E[e]		3.77	8.86	5.55	4.84	4.14	6.7-7.0(m,3) and 7.3-7.8(m,4)
		55.4			70.4	73.7	108.6, 110.3, 114.7, 115.1, 118.5, 121.7 and 130.2(d); 132.5, 145.4, 146.9, 148.3 and 158.7(s)
12F[e]	8.83	3.34	9.33	5.43	4.78	3.88	6.3-6.4(m,3) and 6.7-7.0(m,4)
		55.3			70.5	72.8	101.5, 104.8, 107.5, 110.2, 114.6, 118.4, and 129.4(d); 133.0, 145.3, 146.9, 158.0, and 159.3

a-f, see Table 4 footnotes.

[lit.[13] m.p. 88.0-88.5°]; IR (mull) cm^{-1} 1730 (ester C=O), 1690 (ketone C=O), and 1600 (aryl); ^{1}H-NMR ($CDCl_3$) δ 2.33 (s, 3, Ac), 3.89 (s, 3, $ArOCH_3$), 4.42 (s, 2, CH_2Br), 7.13 (d, 1, J = 8 Hz, aryl), 7.58 (d of d, 1, J = 8 and 2 Hz, aryl), and 7.60 (d, 1, J = 2 Hz, aryl).

1-(4'-Acetoxy-3'-methoxyphenyl)-2-(3"-nitrophenoxy)ethanone (8E). To a stirred mixture of 4.0 g (14 mmoles) of 5, 1.5 g (9 mmoles) of KI, 3.1 g (22.5 mmoles) of K_2CO_3, and 50 mL of dry acetone was added dropwise 2.4 g (17 mmoles) of m-nitrophenol dissolved in 40 mL of anhydrous acetone. The mixture was refluxed for 3 hr, distilled to remove most of the acetone, diluted with 100 mL of water and extracted three times with 50 mL of chloroform. The $CHCl_3$ extracts were combined, washed with 0.5M NaOH and water, dried (anhydrous Na_2SO_4) and evaporated to give a solid residue, 3.8 g (80% yield). Recrystallization from benzene-petroleum ether gave crystals (61.5%), m.p. 130-133°C; IR (mull) cm^{-1} 1760 (ester C=O) 1690 (ketone C=O) and 1600 (aryl); ^{1}H-NMR ($CDCl_3$) δ 2.35 (s, 3, Ac), 3.91 (s, 3, OCH_3, 5.38 (s, 2, $-CH_2-$), and 7.14-7.93 (m, 7, aryl); MS, m/e (%), 345 (M^+, 1) 303 (12), 151 (100), 137 (4), 123 (6), 92 (3), 76 (3), and 65 (3).

1-(4'-Hydroxy-3'-methoxyphenyl)-2-(3"-nitrophenoxy)ethanone (9E). A mixture of 0.32 g (6 mmoles) of sodium methoxide, 1.75 g (5.1 mmoles) of 8E and 20 mL of absolute methanol was refluxed for 2 1/2 hr, cooled, diluted with water and acidified with concentrated HCl to give a precipitate. The suspension was warmed and extracted while warm with $CHCl_3$. The combined warm $CHCl_3$ extracts were washed with water twice and saturated NaCl solution twice, dried (Na_2SO_4) and concentrated. The resulting precipitate was crystallized from absolute ethanol, 0.944 g, m.p. 187.5-189.5; other physical data are given in Tables 3 and 5.

1-(4'-Acetoxy-3'-methoxyphenyl)-2-(3"-acetoxyphenoxy)ethanone (8G). The procedure used was similar to that for the preparation of 8E, except 5 and m-acetoxyphenol[14] were used, along with a silica gel column chromatography product purification. The chromatography, with toluene and toluene-ethyl acetate elution, afforded m-diacetoxy-

TABLE 7

NMR Data for Substituted Ring A Models

Cpd.	$Ar^{A}CH_3$	$Ar^{B}CH_3$	ArOH	ROH	C_1	C_2	Aryl Signals[b]
17c	2.26 2.49		6.49			2.56	6.66(s,1) and 7.58(s,1)
	15.2 21.8				199.8	29.0	118.4 and 133.6(d); 120.8, 129.7, 139.5, and 156.9(s)
18d			9.32			4.62	6.96(d,2) and 7.95(d,2)
					189.8	32.2	115.9 and 131.8 (d); 126.6 and 162.6(s)
19c	2.26 2.49		5.49			4.40	6.67(s,1) and 7.56(s,1)
	15.6 21.8				191.5	34.8	118.8 and 134.3(d); 122.1, 126.1, 140.8, and 159.5(s)
20[e]		2.25	10.44			5.39	6.7-6.9(m,6) and 7.89(d,2)
		21.3			192.3	69.6	111.5, 115.1, 115.3, 121.5, 129.0, and 130.4(d); 125.9, 138.7, 157.9, and 162.4(s)
21[d,e]	2.27 2.41	2.22	8.90			5.23	6.7-6.8(m,4), 7.0-7.2(m,1), and 7.77(s,1)
	15.5 21.2	21.3				70.6	111.4, 115.1, 117.8, 121.2, 128.9, and 132.4(d); 121.0, 125.1, 138.6, 138.6, 157.9, and 158.8(s)

22[d]	2.22 2.42		9.01			5.47	6.77(s,1), 7.2-7.6(m,4), and 7.82(s,1)
	15.4 21.3				193.9	70.6	110.8,[h] 116.9,[h] 117.7, 118.5, 130.2, and 132.4(d); 120.9, 124.6, 129.9,[g] 138.6, 158.1, and 158.8(s)
23[e]		2.25	9.27	5.38	4.78	3.91	6.7-6.8(m,5) and 7.0-7.2(m,3)
		21.0			70.4	72.8	111.2, 114.5, 114.8, 120.8, 127.2, and 128.8(d); 132.3, 138.5, 156.2, and 158.2(s)
24[c,d]	2.26 2.31	2.21	5.33	2.84	5.25	3.96	6.53(s,1), 6.7-6.8(m,3), and 7.1-7.3(m,2)
	15.8 18.7	21.4			69.0	73.4	112.1, 115.8, 116.8, 121.8, 129.3, and 129.6(d); 121.8, 130.9, 133.8, 129.5, 154.7, and 159.5(s)
25[d]	2.17 2.27		8.02	4.51	5.22	4.09	6.63(s,1) and 7.2-7.6(m,5)
	15.9 18.7				68.7	73.8	112.0,[h] 117.0, 117.6,[h] 119.1, 129.3, and 131.0(d); 122.0, 130.4, 131.6,[g] 133.9, 154.9, and 159.8(s)

a-f, see Table 4 footnotes.
[g]Quartet or doublet (J = 0.2 Hz) in the decoupled spectrum; signals probably correspond to C_2" and C_4".

phenol, 4-acetoxy-3-methoxy-α-iodoacetophenone (m.p. 97.5-99.5 from benzene crystallization), and **8G** (7% yield): m.p. 103.5-105.5 (benzene); IR (mull) cm^{-1} 1760 and 1740 (ester C=O), 1710 (ketone C=O), and 1600 (aryl); ^{1}H-NMR ($CDCl_3$) δ 2.28 (s, 3, Ac), 2.34 (s, 3, Ac), 3.89 (s, 3, OCH_3), 5.23 (s, 2, $-CH_2-$), 6.65-6.86 (m, 3, aryl), 7.10-7.36 (m, 3, aryl) and 7.53-7.62 (m, 1, aryl); ^{13}C-NMR ($CDCl_3$) ppm 20.5 and 21.0 (q, Ac methyls), 55.9 (q, OCH_3), 70.6 (t, $-CH_2-$), 108.4, 111.4, 112.1, 114.5, 121.0, 122.7, and 129.6 (d, aryl), 132.7, 132.9, 144.0, 151.3, 158.4 (s, aryl), 167.9 and 168.7 (s, ester C=O) and 192.3 (s, ketone C=O); MS, m/e (%), 358 (M^+, 3), 316 (15), 274 (9), 151 (100), 137 (5), 123 (8), 93 (3), and 65 (4).

1-(4-Hydroxy-3'-methoxyphenyl)-2-(3"-hydroxyphenoxy)ethanone (9F). This compound has been obtained in two ways. The one way employed a procedure similar to the conversion of **8E** to **9E**, namely a hydrolysis of **8E** to **9F**; again solubility problems arose and the yield was low. The other procedure employed the standard coupling reaction of 6 with sodium m-acetoxyphenolate ($7G^-$) with chromatography work-up; small amounts of **9F** were obtained directly from the chromatography, meaning that a transesterification or hydrolysis reaction had occurred. Both procedures gave **9F** of m.p. 145-146 (benzene); physical data are given in Tables 3 and 5.

2,5-Dimethyl-4-hydroxy-α-bromoacetophenone (19). The standard bromination procedure[4] was used to convert 17.2 g of 2,5-dimethyl-4-hydroxy acetophenone (17)[15] to 20.2 g crystals, m.p. 129-131°C (ether) and 1.5 g of solid from evaporation of the ether mother liquor. A ^{1}H-NMR indicated that the crystals were a 70/30 mixture of **19**/17; physical data on **19** are given in Tables 3 and 7.

1-(4'-Hydroxy-3'-methoxyphenyl)-2-(3'-substituted phenoxy)-1-propanol (11A-D). The **11** series compounds were prepared by the standard $NaBH_4$ reduction procedure applied to the corresponding ketones, **10A-D**. Spectral analysis of the crude products (oils) indicated that they were mixtures of diastereomers; infrared spectra showed no carbonyl absorptions and typical OH and aryl absorptions. The NMR spectra indicated no carbonyl functionality (i.e., no peaks at 190-210 ppm in the ^{13}C-NMR and no downfield

proton aryl signals in the ^{1}H-NMR). Their mass spectra all displayed prominent m/e 153 signals, indicative of fragmentation between C_1 and C_2 with charge retention on C_1.[16] Specific interpretations of the spectral data follow.

m-CH_3 (11A). Reduction of 2.0 g of 9A with 2.6 g (40 equiv.) of $NaBH_4$ gave 2.3 g of oil, still containing small amounts of EtOH. Extensive evaporation removed nearly all of the EtOH. The oil is approximately a 60/40 ratio of isomers, based on ^{1}H-NMR. The oil was dissolved in warm toluene and placed on a silica gel column (2 x 38 cm). Elution of the column with 150 mL of toluene, 400 mL of 2% ethylacetate-toluene, 400 mL of 5% mixture and 250 mL of 10% mixture led to 18 fractions, which were combined into two main fractions, namely 1-7 and 8-16. The former was a 60/40 ratio and the latter a 30/70 ratio of isomers, based on ^{1}H-NMR. Comparison of the ^{13}C-NMR of the fractions allowed several of the signals to be assigned to each isomer. The ^{1}H-NMR ($CDCl_3$, δ) showed 1.10 and 1.18 (d, 3, J = 6 Hz, C_3-methyls), 2.32 (s, 3, aryl methyl), 3.88 (s, 3, OCH_3), 4.3-4.7 (m, 2, C_1 and C_2 protons), 5.67 and 5.70 (s, 1, ArOH), 6.7-7.2 (m, 7, aryl) and 1.7, 2.6, 3.1, and 4.9 (broad s, 1.7, ROH and impurities). The ^{13}C-NMR ($CDCl_3$, ppm) showed 13.1, 15.8, and 21.4 (q, C_3 and aryl CH_3), 55.8 (q, OCH_3), 75.0, 77.8, 77.9, and 78.9 (C_1 and C_2 among the $CDCl_3$ signals), 108.9, 109.4, 112.9, 113.0, 114.0, 117.0, 119.2, 120.5, 122.0, 122.1, and 129.2 (d, aryl), 131.6, 132.0, 139.5, 144.8, 145.4, 146.3, 146.4, 157.2, and 157.4 (s, aryl). The MS, m/e (%), showed 288 (M, 6), 153 (100), 151 (15), 136 (42), 135 (16), 125 (21), 108 (10), 91 (26), 77 (8), 65 (20).

m-Cl (11B). A 0.60 g sample containing 60% 9B and 40% 9H was reduced with 0.88 g (14 equiv.) of $NaBH_4$ to give 0.74 g of oil. The ^{1}H-NMR ($CDCl_3$, δ) showed 1.11 and 1.21 (d, J = 6 Hz, 3, C_3-methyls of the diastereomers, 60/40 ratio), 3.90 (s, 3, OCH_3), 4.2-4.9 (m, 2, C_1 and C_2-protons), 5.62 and 5.69 (s, 1, ArOH, 40/60 ratio), 6.7-7.3 (m, 7, aryl) and 1.5, 2.4 and 2.9 (broad s, 1.2, ROH and impurities). The ^{13}C-NMR ($CDCl_3$, ppm) was quite complex with 13.2, 13.4, and 15.8 (q, C_3-methyls), 55.9 (s, OCH_3), nine signals at 75.0-79.2 (C_1 and C_2, plus $CDCl_3$), fifteen signals at

108.8-130.1 (d, aryl) and thirteen signals at 131.2-158.1 (s, aryl). The MS, m/e (%), showed 308 (M^+ for 11B, 2%), 274 (M^+ for 11H, 2%), 153 (100), 125 (10), 93 (25), 77 (12) and 65 (12).

[The presence of the H (proton) compounds in the B (m-Cl) compounds was not easily seen initially. There are practically no chemical shift differences for the ring A and aliphatic protons and carbons in the NMR spectra; exceptions are the carbonyl carbons of the 9 and 10 compounds. In ^{1}H-NMR, the presence of H or Cl on ring B also has little effect on the other ring B protons except, of course, the number of protons differ. The real clues that H compounds are in some B compounds come from the mass spectral differences, the ^{13}C-NMR carbonyl differences and increased numbers of signals, and in the ^{1}H-NMR phenolic hydroxyl signals and aryl integration.]

m-OCH_3 (11C). Reduction of 1.19 g of 9C gave 1.38 g of oil, containing some ethanol (based on NMR). Attempted crystallization from EtOH/H_2O was unsuccessful. Water was added to the crystallization solvents and the product was extracted with $CHCl_3$. The ^{1}H-NMR showed two sets of signals which indicated that the oil was approximately a 2:1 mixture of diastereomers; these signals were at 5.76 and 5.73 (ArOH, singlets) and 1.11 and 1.19 δ (methyl doubtlets, J = 6 Hz). The ^{1}H-NMR ($CDCl_3$, δ) also showed 3.77, 3.78, and 3.87 (s, 6, OCH_3), 4.3-4.7 (m, 2, C_1 and C_2 protons), 6.5-6.6 (m, 3, aryl), 6.8-7.0 (m, 3, aryl), 7.1-7.3 (m, 1, aryl), 2.6, 3.1, and 4.9 (broad s, 1^+, ROH) and residual ethanol. The ^{13}C-NMR ($CDCl_3$, ppm) showed 13.2 and 15.7 (quartets, C_3-methyls of diastereomers, 35/65 ratio), 55.2 and 55.8 (q, OCH_3), 74.8, 77.7, and 78.7 (C_1 and C_2-carbons mixed with $CDCl_3$ signals), 102.5, 106.5, 106.6, 108.0, 108.1, 108.7, 109.2, 114.0, 119.0, 120.3, and 129.7 (d, aryl), 131.4, 131.8, 144.7, 145.3, 146.2, 146.3, 158.3, 158.5, and 160.5 (s, aryl). The MS, m/e (%), showed 304 (M^+, 5), 153 (100), 152 (32), 151 (32), 125 (30), 124 (19), 123 (10), 107 (17), 93 (59), and 77 (46).

m-CF_3 (11D). Reduction of 0.30 g of 9D gave 0.28 g of oil. Crystallization from EtOH/H_2O was not successful. The ^{1}H-NMR

($CDCl_3$, δ) showed 1.13 and 1.24 (d, J = 6 Hz, C_3-methyls, ca. 60/40 ratio), 3.90 (s, OCH_3), 4.3-4.9 (m, C_1 and C_2 protons), 6.9-7.4 (m, aryl) and 2.0 and 5.6 (v. broad, hydroxyls). The ^{13}C-NMR ($CDCl_3$, ppm) showed 13.5 and 15.7 (q, C_3-methyls, ca. 30/70 ratio), 55.8 (q, OCH_3), 75.2, 77.6, 78.2, and 79.1 (C_1 and C_2 mixed in with $CDCl_3$ signals), 108.9, 109.2, 112.8, 112.9, 114.0, 114.1, 117.6, 117.8, 119.2, 120.2, and 129.8 (d, aryl), 131.2, 145.0, 145.5, 146.3, 146.4, and 157.5 (s, aryl), and 131.7 (q in coupled and decoupled spectra, $\underline{C}-CF_3$. The MS, m/e (%), showed 342 (M^+, 10), 181 (11), 153 (100), 151 (9), 145 (7), 125 (14), 93 (23), and 65 (10).

4-Hydroxy-3-methoxy-β-(m-methylphenoxy) styrene (27, R=CH_3, Fig. 2). In each of 14 small pressure vessels (bombs) was placed 30 mg (0.11 mmol) of 12A and 18 mg (0.33 mmol) of sodium methoxide dissolved in 3.5 mL of abs. methanol. The latter solution was pipetted into the bombs in a nitrogen filled glove bag. The bombs were sealed (under N_2), rotated in an oil bath at 150°C for 5 hours, cooled, opened, and combined by pouring the contents and 3 water washes into a separatory funnel. The solution was acidified to pH 3 with 0.5M HCl and extracted 3 times with $CHCl_3$. The combined $CHCl_3$ extracts were dried (Na_2SO_4) and evaporated. A GC analysis of the residue showed a cis and trans mixture of the desired product, m-cresol, and some minor impurities.

The residue was purified by chromatography through a 2.5 cm diameter, 35 cm tall column of basic (9.5-10.6 pH) alumina packed in toluene. [A previous experiment using a silica gel column led to partial degradation of vinyl ether products.] The elution sequence, leading to 40 fractions, consisted of 200 mL of toluene, followed by ethyl acetate (%)/toluene mixtures: 200 mL (1%), 100 mL (2.5%), 100 mL (3%), 100 mL (4%), 100 mL (5%), 100 mL (6%), 100 mL (10%), 200 mL (15%) and 600 mL (20%). Fractions were analyzed by GC and a few by GC/MS and NMR.

Fractions 26-32 were combined to give roughly a 60/40 mixture of cis/trans-27 (R=CH_3): ^1H-NMR ($CDCl_3$) δ 2.35 (s, 3, $ArCH_3$), 3.88 (s, 3, $ArOCH_3$), 5.53 (d, J = 7 Hz, 0.6, cis $C_\alpha H$), 5.58 (s,

0.4, exchangeable, trans ArOH), 5.62 (s, 0.6, exchangeable, cis ArOH), 6.26 (d, J = 12 Hz, 0.4, trans $C_\alpha H$), 6.51 (d, J = 7 Hz, 0.6, cis $C_\beta H$), 6.8-7.4 (m, ~ 10, trans $C_\beta H$, ArH, and $CHCl_3$); ^{13}C-NMR ($CDCl_3$) PPM 21.3 (q, $ArCH_3$), 55.6 and 55.7 (q, $ArOCH_3$), 108.0-129.1 (numerous singlet and doublets, aryl and vinyl-C_α), 139.6 and 139.7 (d, C_β), and 141.7-156.9 (six signals, singlets, $C_{Ar}OR$); MS, m/e (%), 256, (M, 100), 241 (7), 227 (14), 195 (12), 133 (18), 91 (10), and 65 (13).

Degradation Procedure. The model degradations were conducted in 4-mL capacity pressure vessels (bombs). The bombs, as many as 14 at a time, were mounted on a metal plate, which was rotated in an oil bath by means of a chain-drive system and stirring motor. The rotation could be stopped at various times to remove bombs.

The bombs were filled and sealed in a nitrogen atmosphere (glove bag). All solutions were prepared in a glove bag using deoxygenated, distilled water. All reactant solutions, IS solutions, etc., were added with an automatic pipette.

Standard solutions of sodium hydroxide and model compounds and p-isopropylphenol (IS) in aq. NaOH were prepared just prior to use. The models were present in 0.015 mmole amounts and the other reagents were adjusted to 0.015 mmole = 1 equiv.

The appropriate solutions and make-up water were added to the cool bombs. After heating for specific lengths of time, the bombs were removed from the hot oil bath, immediately cooled in ice-water, opened, diluted with IS solution, and the contents transferred to an Erlenmeyer flask for derivatization, followed by GC analysis. Several 1M NaOH and water washes of the bombs were used to ensure quantitative transfer.

Methylation. Dimethylsulfate (1 mL, 100-350 equiv./model) was added to the product/IS mixture, and the solution was stirred rapidly for 15 min in a loosely stoppered Erlenmeyer flask. Concentrated ammonium hydroxide (4.5 mL) was added to quench the excess Me_2SO_4, and the solution was stirred another 15 min. Chloroform (2 mL) was added, and the solution was stirred vigorously for 2 min. The $CHCl_3$ phase was then removed with a disposable pipette, dried over

Na_2SO_4 and analyzed by G.C. [Additional $CHCl_3$ extractions gave the same ratio of products to IS at a much more dilute concentration, and were thus not useful.]

Benzoylation. In this case the bombs were washed three times with 1.5 mL 1M NaOH and twice with 1.5 mL toluene. Benzoyl chloride (21 L, roughly 5 equiv./model) and 8 mg (0.4 equiv./model) of benzyltributylammonium bromide were added to the Erlenmeyer containing the base solution, toluene and a stir bar. After stirring for 30 min, the aqueous layer was pipetted off, and the organic layer was washed twice with 3 mL 1M NaOH, twice with water, dried over Na_2SO_4, and analyzed by G.C.

Just as in the methylation procedure, reagent amounts and conditions were adjusted to give maximum, reproducible derivatization. Standard mixtures of phenols were also derivatized to give samples for determining G.C. response factors.

Analysis. Analysis of product mixtures for their phenol content was done on a 5890 Hewlett Packard gas chromatograph using a 6 foot 1/4-inch glass column packed with 3% silicone OV-17 on 100/120 chromosorb W-HP. The following temperature program was used: 65° (2 min), then 2°/min to 80° (3 min) and then 30°/min to 285° (4 min).

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