Distillation of the residue at reduced pressure gave the product: 3.45 g, 66%; bp 126–128 °C (20 mmHg); ^{1}H NMR ($CDCl_3$) δ 0.1 (sh t, 9, $SnMe_3$), 1.1–2.1 (br m, 10, CH_2, CHSn, and OH), 3.5 (br s, 1, CHO). Anal. Calcd for $C_9H_{20}OSn$: C, 41.11; H, 7.67; Sn, 45.15. Found: C, 41.64; H, 7.80; Sn, 46.02.

***cis*-2-(Trimethylstannyl)cyclohexyl Acetate (3-OAc).** *cis*-2-(Trimethylstannyl)cyclohexanol (0.26 g, 1.0 mmol) and pyridine (0.08 g, 1.1 mmol) were dissolved in 1 mL of dry ether cooled to 0 °C. With stirring, acetyl chloride (0.08 g, 1.1 mmol) was added dropwise. The mixture was then allowed to warm to room temperature and was stirred overnight. The solution was filtered through a glass wool plug to remove solid product. The filtrate was washed with a cooled saturated aqueous $CuSO_4$ solution and with a 10% $NaHCO_3$ solution and was dried ($MgSO_4$). Rotary evaporation of the solvent gave an oil: ^{1}H NMR ($CDCl_3$) δ −0.3, 0.1, 0.4 (sh t, 9, $SnMe_3$), 0.7–2.1 (m, 9, CH_2 and CHSn), 2.0 (s, 3, $COCH_3$), 5.1 (m, 1, CHO); IR (mull) 1736 cm^{-1} (C=O).

***r*-5-*tert*-Butyl-*cis*-2-(trimethylstannyl)cyclohexan-*trans*-ol (5-OH).** Under N_2 atmosphere, a solution of chlorotrimethyltin (4.0 g, 20 mmol) in 20 mL of anhydrous THF was added dropwise to a mixture of Li wire (1.4 g, 0.2 mol) and 50 mL of dry THF cooled with an ice bath. After 24 h, a solution of *trans*-4-*tert*-butylcyclohexene oxide[2] (3.1 g, 20 mmol) in 10 mL of THF was added dropwise to the mixture, which was then cooled with an 2-propanol–dry ice bath. The solution was stirred at room temperature overnight, and the excess Li was removed by filtration. The filtrate was washed with H_2O (3 × 50 mL). The mixture was dried over $MgSO_4$, and the solvent was evaporated to provide a solid that was recrystallized in pentane: 3.45 g, 53%; mp 54–56 °C; ^{1}H NMR ($CDCl_3$) δ −0.1, 0.1, 0.3 (sh t, 9, $SnMe_3$), 0.8 (s, 9, CH_3), 1.0–2.0 (br m, 8, CH_2 and CH), 4.3 (br s, 1, CHO).

Solvents and Conductometric Measurements. See ref 2.

Kinetics (^{1}H NMR Measurements of the Acid-Catalyzed Elimination of the Alcohols). A JEOL FX-270 NMR spectrometer was used in the variable temperature mode. The probe was adjusted to the desired temperature before insertion of the sample tube. At least 5 min was allowed for thermal equilibration for runs above room temperature. In case of low-temperature runs, the solvent was cooled to −78 °C in a NMR tube before the sample was added. About 10–20 spectra were recorded at a desired time interval. Spectra were saved on floppy disks and processed later. For the calculations, either the increase of the peak at δ 5.8 (vinyl proton of product cyclohexene) or the decrease of the peak at δ 4.2 (for cis alcohols) or δ 3.5 (for trans alcohols) could be used. For the germyl-substituted substrates, increase of the sharp singlet at δ 0.8 or decrease of the sharp singlet at δ 0.1 could be conveniently monitored. The solvent peak was used as reference to assure that integrations were all on the same scale.

Electron-Transfer Reactions in Pulping Systems. 5. Application of an Intramolecular Cyclization Reaction as a Detector of the Formation of Quinonemethide Radical Anions

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Compound **6**, which incorporates a hex-5-enyl group on a quinonemethide precursor, has been synthesized and reacted in 1 M NaOH at 135 °C in the presence of various pulping additives. Reduction of **6** either prior to or after cyclization to a five-membered ring provides evidence that a quinonemethide radical anion intermediate had formed. Some additives such as anthrahydroquinone and glucose were effective electron-transfer agents for the probe quinonemethide, while others such as sodium sulfide and sulfite were ineffective. The probe, therefore, provides information on the nature of chemical reactions that may be occurring during the pulping of wood. Anthrahydroquinone and glucose provided significantly different amounts of cyclized products. Glucose gave high yields of cyclized products, including three unique tricyclo[7.3.0.0^{2,7}]dodecatrienes. Apparently glucose reduces the radical intermediates relatively slowly, providing time for cyclization to occur. With no additives, other than 1 M NaOH, and long reaction times, the probe compound **6** provided some cyclized products; the electron-transfer agent in this case presumably is a phenolate ion.

Introduction

The rapid rates observed during anthraquinone (AQ) pulping have generally been attributed to the ability of anthrahydroquinone (AHQ), a reduced form of AQ, to promote lignin fragmentation reactions.[1-5] One proposed mechanism for the fragmentation process is that AHQ^{2-} adds to a quinonemethide (QM), forming a QM–AHQ^{2-} adduct, which subsequently undergoes an elimination reaction, producing fragmented products and AQ. Simple adducts of model compounds have been prepared and shown to exhibit this kind of chemistry.[2-5] However, since adduct formation reactions are reversible,[6] it is not clear whether adducts are key intermediates to fragmentation or just part of side reactions.

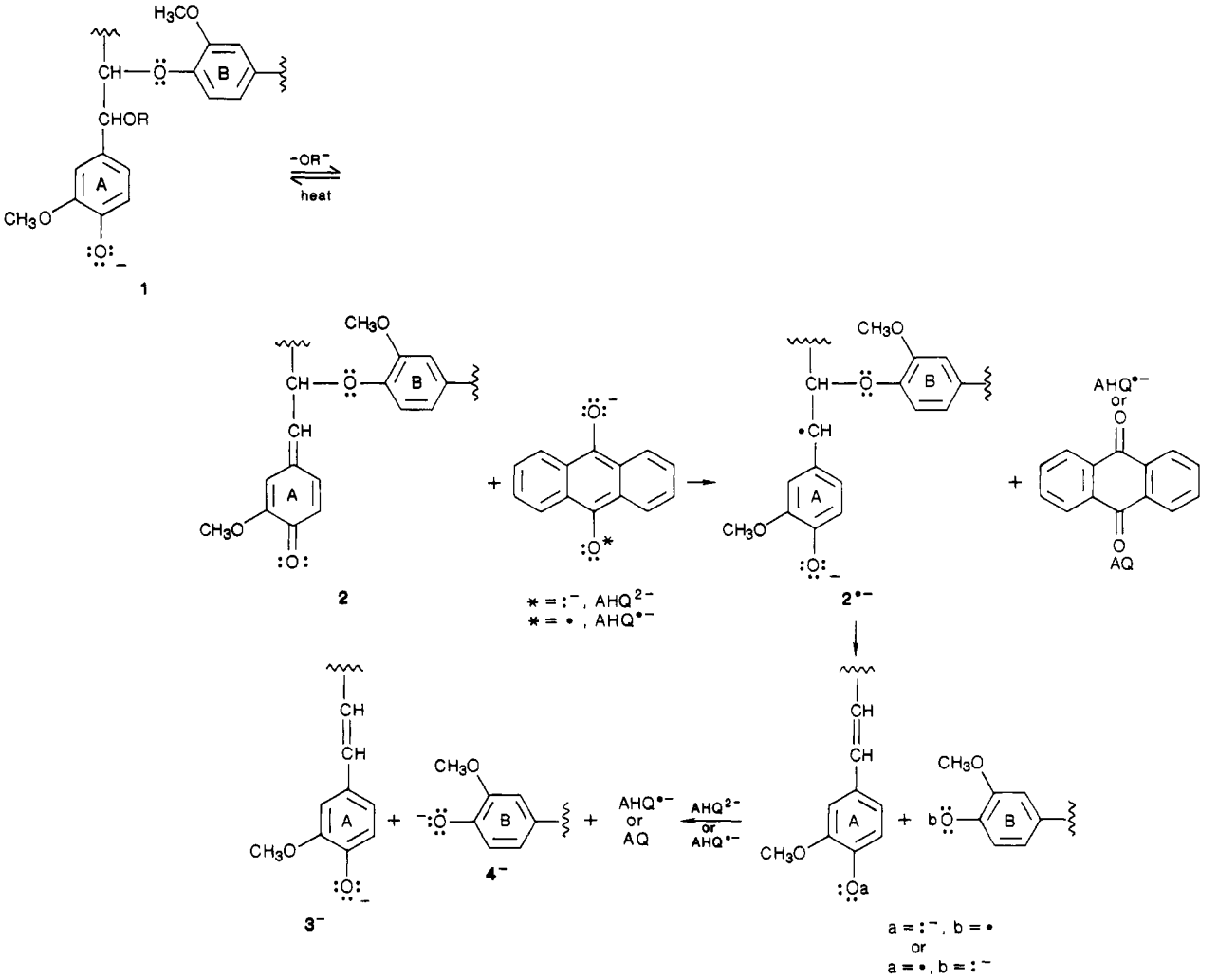
An alternative mechanism for an AHQ-induced lignin fragmentation process is one involving reduction of quinonemethides by AHQ ions via electron-transfer processes (Scheme I).[1] For simplicity, the electron-transfer steps are shown here, and in other drawings, as single steps. This may or may not be the case, as will be discussed later.

Quinonemethides are generated when phenolic lignin polymer end units, which have leaving groups at the para α-carbon, are heated, i.e., **1** → **2**. The QM **2** shown in

(1) Dimmel, D. R. *J. Wood Chem. Technol.* **1985**, *5*, 1 and references cited therein.
(2) Obst, J. R.; Landucci, L. L.; Sanyer, N. *Tappi* **1979**, *62*(1), 55.
(3) Landucci, L. L. *Tappi* **1980**, *63*(7), 96.
(4) Gierer, J.; Lindeberg, O.; Noran, I. *Holzforschung* **1979**, *33*, 213.
(5) Aminoff, H.; Brunon, G.; Miksche, G. E.; Poppius, K. *Paperi Puu* **1979**, *61*, 441.
(6) Dimmel, D. R.; Shepard, D. *J. Org. Chem.* **1982**, *47*, 22.

0022-3263/88/1953-5428$01.50/0

Scheme I. Delignification via AHQ-Induced SET Reactions



Scheme I contains a labile C_β-aryl ether bond; such bonds contribute 50–60% of interunit linkages in lignin.[7] The A units on the structures in Scheme I represent the aromatic ring or quinonemethide unit in a terminal monomer unit of lignin; B is the aromatic ring in the second monomer in the chain.

Fragmentation of lignin by electron transfer (Scheme I) is viewed as beginning with a transfer of an electron from an electron-rich AHQ^{2-} to an electron-poor QM, producing $AHQ^{\bullet-}$ and a quinonemethide radical anion ($2^{\bullet-}$). The $QM^{\bullet-}$ then fragments to a phenolate ion and a phenoxy radical; a second electron-transfer converts the phenoxy radical to a phenolate ion. The two proposed phenolate ion products, **3** and **4**, are the same ones observed when QM–AHQ adducts are heated in alkali.[2-5]

Evidence supporting an electron-transfer fragmentation process (Scheme I) has been provided by observing the cleavage of a relatively stable β-aryl ether QM in the presence of electrochemically generated AHQ ion radicals.[9] The study, however, employed conditions quite different from pulping; the temperature was ambient and the solvents were principally organic.

Studies aimed at defining the exact nature of the QM/AHQ interaction have been hampered by the fact that formation of the QM species is the rate-determining step for fragmentation.[9-12] The use of clock reactions, however, has demonstrated that AHQ is superior to other reagents at causing β-aryl ether cleavage,[13] implying that its chemistry is different than the usually accepted adduct chemistry exhibited by other additives.

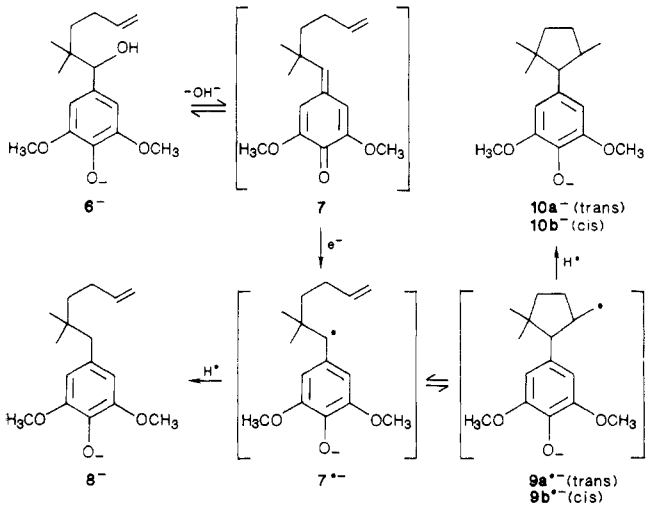
In order to determine if certain reagents can electron-transfer to lignin model quinonemethides under conditions similar to alkaline pulping (1 M NaOH and 170 °C), we have synthesized and studied the alkaline reactions of a compound that is soluble in alkali, can form a QM, and can show the existence of a radical intermediate. The reaction of the compound with chemicals typically present during pulping, such as AHQ, carbohydrates, sulfite, and sulfide, is the subject of this report.

Results

Cyclization of hex-5-enyls to five-membered rings is generally assumed to be diagnostic of the intermediacy of radicals in reaction mechanisms.[14,15] A compound con-

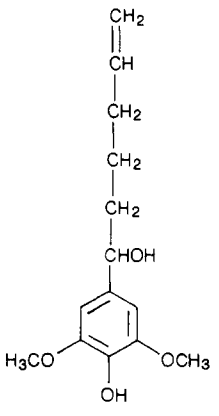
(7) Adler, E. *Wood Sci. Technol.* **1977**, *11*, 169.
(8) Dimmel, D. R.; Perry, L. F.; Palasz, P. D.; Chum, H. L. *J. Wood Chem. Technol.* **1985**, *5*, 15.
(9) Dimmel, D. R.; Schuller, L. F. *J. Wood Chem. Technol.* **1986**, *6*, 345.
(10) Dimmel, D. R.; Schuller, L. F. *J. Wood Chem. Technol.* **1986**, *6*, 535.
(11) Dimmel, D. R.; Schuller, L. F. *J. Wood Chem. Technol.* **1986**, *6*, 565.
(12) Miskche, G. E. *Acta Chem. Scand.* **1972**, *26*, 4137.
(13) Dimmel, D. R.; Schuller, L. F.; Apfeld, P. B. *J. Wood Technol.* **1987**, *7*, 97.
(14) Garst, J.; Pacificia, J.; Lamb, R. *J. Am. Chem. Soc.* **1966**, *88*, 4260.
(15) Walling, C.; Cooley, J. H.; Ponaras, A. A.; Racah, E. J. *J. Am. Chem. Soc.* **1966**, *88*, 5361.

Scheme II. Reactions of Compound 6

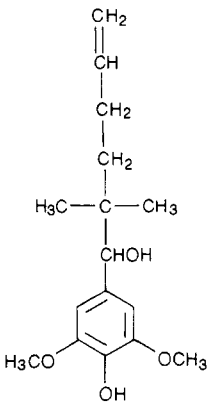


taining a hex-5-enyl group and substituents necessary for QM formation, namely, a free phenol and a leaving group at the α-carbon of a para side chain, was sought to determine if electron-transfer to QMs is possible under pulping-like conditions. Model compound **5**, which meets the desired criteria, was easily prepared by the Grignard reaction of 5-bromo-1-pentene with syringaldehyde. Unfortunately, the alkaline reactions of **5** at 135 °C resulted in only dehydration, yielding styrene products; even addition of AHQ did not prevent dehydration.

A second model (**6**) was prepared with methyl groups at the β-position. Besides blocking dehydration, these methyl groups have the additional benefit of increasing the rate of cyclization.[16] Synthesis of **6** was accomplished by converting 5-chloro-5-methyl-1-hexene to a Grignard reagent and mixing the latter with syringaldehyde. The expected reactions of **6** are shown in Scheme II.



5



6

NaOH Reactions. The reaction of **6** in 1 M NaOH at 135 °C for 4 h provided only low yields of 2,6-dimethoxyphenol (syringol). Syringol was always observed as a product when **6** was reacted in hot alkali. The mechanism of formation of syringol probably involves a reverse aldol reaction from a keto form of the phenol **6**; its formation does not appear to be related to electron-transfer. When the reaction time was increased to 18 h, small yields of cyclized compounds **10a** and **12–14** were observed (Table I). Scheme III shows compounds **12–14** and a possible route to their production.

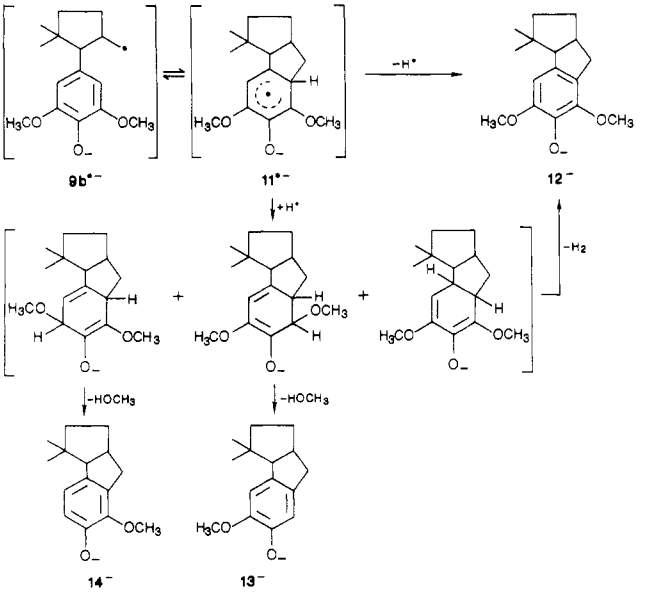
(16) Beckwith, A. L. J.; Lawrence, T. *J. Chem. Soc. Perkin Trans. 2* **1979**, 1535.

Table I. Crude Product Yields from the Reactions of 6 in 1 M NaOH at 135 °C[a]

	relative gas chromatograph area percentages[b]		
product (M^+)[c]	no additive 18 h	2 equiv AHQ 2 h	5 equiv glucose 18 h
syringol (154)	8.4	6.0	5.1
14 (232)	1.4		10.0
13 (232)	1.4		7.3
10a (264)	4.7	5.5	50.5
10b (264)		3.2	2.7
8 (264)	trace	69.0	1.8
12 (262)	5.8	*e*	5.1
a (262)[d]			
c (264)			2.8
6 (280)	61.9	6.9	11.9
d (280)		3.1	
b (280)	8.8		
e (280)		4.2	
total	92.4[f]	97.9[f]	97.2[f]

[a] Comparison of gas chromatograms is available as supplementary material; see paragraph at the end of the paper. [b] Yields are based on integrated signal areas, with no reference to an internal standard. [c] The number in parentheses refers to the apparent molecular mass based on EI mass spectral data; compounds are presented in increased order of GC elution. [d] Unknown which overlaps with **12** in the no additive case. [e] Appears to be absent, but the region is dominated by a signal from AQ. [f] The difference from 100% reflects broad signal areas not assigned.

Scheme III. Formation of Additional Cyclization Products



Anthrahydroquinone Reactions. When 2 equiv of AHQ were present during the heating of **6** at 135 °C in aqueous alkali, two products (**8** and **10**) were observed in good yields in less than 2 h (Table I). In contrast to the NaOH reaction, very little starting material remained after 2 h. The major product in the AHQ reaction was the acylic compound **8**. The simple cyclized compound **10**, existing as roughly a 5:3 mixture of isomers, was only present in small amounts; the more extended cyclized compounds **12–14** were absent.

Other Pulping Reagents. Two other compounds used to aid delignification, sodium sulfide and sodium sulfite, were also tested for their ability to transfer electrons to the quinonemethide derived from **6**. Neither of these inorganics provided any increase in cyclized products as compared to the reaction of **6** with no additives. Even at 170 °C, sulfide displayed no ability to electron-transfer. The inability of sulfide to transfer electrons is in agreement

Table II. ^{13}C NMR Spectral Data for 6 and the Products Formed from the Reaction of 6 in 1 M NaOH at 135 °C[a]

C	6	8	10a	12	13	14
C_1	81.0[c] (d)	48.3 (t)	64.8 (d)	61.5 (d)	61.5 (d)	59.7 (d)
C_2	*b*	34.1 (s)	42.4 (s)	44.8 (s)	*b*	*b*
C_3	38.0 (t)	28.7 (t)	40.5 (t)	38.1 (t)	40.9 (t)	38.5 (t)
C_4	28.4 (t)	40.8 (t)	31.0 (t)	32.2 (t)	32.3 (t)	32.2 (t)
C_5	139.2 (d)	139.2 (d)	37.4 (d)	43.6 (d)	43.8 (d)	43.9 (d)
C_6	113.6 (t)	113.6 (t)	19.6 (q)	42.6 (t)	42.6 (t)	42.5 (t)
gem-Me_2	22.9 (q)	26.9[c] (q)	24.5 (q)	24.9 (q)	25.2 (q)	24.9 (q)
	23.0 (q)		29.4 (q)	30.1 (q)	30.2 (q)	29.9 (q)
$C_{1'}$	133.6 (s)	133.7 (s)	133.0 (s)	136.4 (s)	127.1 (s)	134.6 (s)
$C_{2'}$	104.5 (d)	107.2 (d)	105.9 (d)	128.0 (s)	144.5 (s)	137.8 (s)
$C_{3'}$	146.0 (s)	146.1 (s)	146.3 (s)	146.3 (s)	109.9 (d)	142.2 (s)
$C_{4'}$	132.9 (s)	132.8 (s)	131.6 (s)	135.5 (s)	145.0 (s)	146.4 (s)
$C_{5'}$	146.0 (s)	146.1 (s)	146.3 (s)	142.4 (s)	135.6 (s)	113.2 (d)
$C_{6'}$	104.5 (d)	107.2 (d)	105.9 (d)	103.6 (d)	107.8 (d)	120.5 (d)
OCH_3	56.2[c] (q)	56.2[c] (q)	56.2[c] (q)	56.4 (q)	56.3 (q)	60.6 (q)
				59.7 (q)		

[a] The numbering system begins with the benzyl carbon as 1 and its attachment to the ring at the 1′ carbon. [b] Not observed. [c] Represents two methyls (strong peak).

with past research[17] and other recent studies.[18]

Carbohydrate Reactions. Both soluble and insoluble carbohydrates are present during the pulping of wood. Fullerton and Wilkins have shown that the fragmentation of β-aryl ether lignin models is promoted by sugars having a free aldehyde group or cyclic hemiacetal structure which is in equilibrium with an aldehyde.[19] They proposed that in alkali the enolate ion of the aldehyde is formed and adds to a quinonemethide to give an adduct which, when heated, undergoes β-aryl ether fragmentation; such reactions were demonstrated to occur with L-ascorbic acid. Sugars that had no available aldehyde groups, and therefore could not form enolate ions, were ineffective at promoting β-aryl ether cleavage.

The reaction of probe compound **6** with 5 molar equiv of glucose in 1 M NaOH was studied. A fairly large excess of glucose was used because of the short lifetimes of glucose in alkali at high temperatures.[20] As can be seen in Table I, the major product from an 18-h reaction between glucose and **6** was the cyclized compound **10a**. Also formed were the acyclic compound **8** and the cyclic compounds **12**, **13**, and **14**. When compared to AHQ addition, the yield of **8** was greatly decreased, while the yields of cyclized compounds **10** and **12–14** were substantially increased.

The reactions of probe **6** with two sugars that have acetal functional groups, and therefore no directly available aldehyde, were compared to that of glucose, which is an aldehyde. Both sugars gave much less cyclized products. With methyl α-D-glucopyranoside, roughly a 75% yield of starting material and a 15% yield of cyclized products were present after a 18-h reaction time at 135 °C. For methyl β-glucopyranoside, 54% starting material and 36% cyclized products were observed after reaction for 18 h. The greater reactivity of the β derivative is in accord with its faster conversion to an aldehyde in aqueous alkali.[21] It is apparent that a free aldehyde is necessary for good electron transfer.

Product Characterization. Column chromatography was employed to isolate a small sample of acyclic product **8** from the AHQ reaction of **6**; the sample was readily characterized by spectral means. Likewise, small samples of cyclized products **10** and **12–14** were isolated from the glucose reactions and characterized. The NMR chemical shifts and C_α coupling constant of **10** isolated from the glucose reaction indicated a high predominance of the trans isomer **10a** (~95:5) over the cis isomer **10b**. As can be seen in Table I, the AHQ reaction gives comparable amounts of the cis and trans isomers, with the latter being present to a somewhat greater extent.

The NMR spectra of crude product mixtures contained principally the signals of the components indicated by the GC analysis. In other words, the chromatography procedures did not alter the product mixtures to any appreciable extent and there were no major "hidden" components in the mixtures.

Table II presents the ^{13}C NMR spectral data for **6** and its reaction products. The data clearly support the structural assignments; ^1H NMR and MS data lend additional support (see Experimental Section). Distinguishing spectral features for cyclized products **10** and **12–14** are the lack of olefinic carbons and a corresponding increase in aliphatic carbons. The symmetry of the aryl rings for **6** and **8** is apparent from the spectra. The number and position of the aryl CH carbons differentiates compounds **12–14**; the two upfield aryl CH carbons in **13** indicate two protons ortho to oxygen aryl substitutents, while **14** has only one of this type. The difference in the number of methoxy groups in compounds **13** and **14** is also distinguishing.

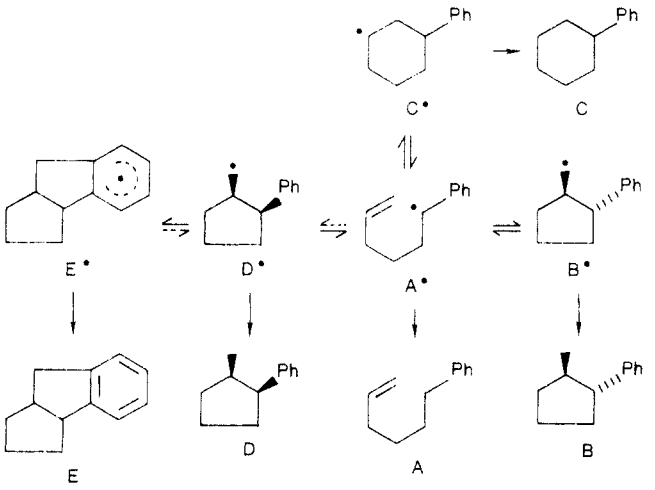
Discussion and Conclusions

The production of cyclization products from high temperature reactions of compound **6** indicates that the quinonemethide radical anion $\mathbf{7}^{\bullet-}$ had been produced. The rationale for how $\mathbf{7}^{\bullet-}$ accounts for the observed products is based on literature precedence and is believed to follow the steps shown in Schemes II and III. How $\mathbf{7}^{\bullet-}$ is generated, and what alternative intermediates could be present, will be discussed later.

Benzyl radicals with an attached pentenyl group are known to interconvert with cycloalkyl radicals. Walling and Cioffari[22] generated the radicals A•, B•, C•, and D• (Scheme IV) from reaction of the corresponding bromides with tributylstannane or triethylsilanes. The radicals interconvert to some extent; D• gives all of the other radicals, including E•; radicals A–C apparently give no D• or E•. However, Pines and co-workers used another method of generating radical A• and observed B, C, D, and E as products.[23] [Product distributions and the extent of in-

(17) Gierer, J. *Wood Sci. Technol.* **1985**, *19*, 289.
(18) Smith, D. A. Doctoral Dissertation, The Institute of Paper Chemistry, Appleton, WI, June, 1986.
(19) Fullerton, T. J.; Wilkins, A. L. *J. Wood Chem. Technol.* **1985**, *5*, 189.
(20) Green, J. W.; Pearl, I. A.; Hardacker, K. W.; Andrews, B. D.; Haigh, F. C. *Tappi* **1977**, *60*(10), 120.
(21) Janson, J.; Lindberg, B. *Acta Chem. Scand.* **1959**, *13*, 139.
(22) Walling, C.; Cioffari, A. *J. Am. Chem. Soc.* **1972**, *94*, 6064.

Scheme IV. Interconversion of Benzyl and Cycloalkyl Radicals



terconversions will depend on the rates of the R• + R'H → RH + R'' quenching reactions.]

Both the previously cited investigations report a kinetic preference for the open radical A• to cyclize to a five-membered ring instead of a 6-membered ring.[22,23] Under one set of conditions[22] the open radical A• cyclized exclusively to the *trans*-1-methylcyclopentane (B); while in the other case,[23] radical A• gave both *trans*- and *cis*-1-methylcyclopentane (B and D) in 5:3 to 6:1 ratios. Cyclization of aliphatic radicals is reported to occur with high cis stereospecificity.[24]

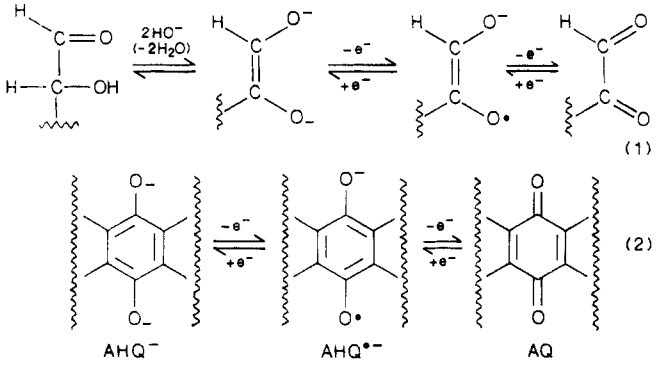
Both previous investigations of benzyl radical cyclizations indicated that a second cyclization occurred when radical E• was present to give 1,2,3,3a,8a-hexahydrocyclopent[*a*]indene (E).[22,23] Surzur and Stella also report an example of two successive radical cyclizations involving an olefinic double bond and an aromatic ring.[25]

Clearly, our results parallel these literature examples. We observe a high preference for cyclization of $7^{\bullet-}$ to cyclopentane-type products; the corresponding cyclohexane products should have similar volatilities, yet were not observed. The *gem*-dimethyl groups must be playing a role in the prevention of interconversion of cyclopentylmethyl radicals and cyclohexyl radicals; Walling and Cioffari[22] claim that such an interconversion in their case proceeds without the intermediacy of the open-chain radical.

The AHQ^{2-} reactions of **6** appear to have a good hydrogen atom donor in the system; this may be the monoprotonated versions of AHQ^{2-} and $AHQ^{\bullet-}$, i.e., AHQ-H$^-$ and AHQ-H•. Much of the $7^{\bullet-}$ formed from **6** must be rapidly trapped by the H-atom donor, such as AHQ-H$^-$ + R• → $AHQ^{\bullet-}$ + RH, giving rise to a high yield of open-chain product **8**. Few cyclization products are formed because the rate of cyclization must be slower than radical quenching. The extent of *trans*- and *cis*-2-methyl-1-syringylcyclopentane (**10a** and **10b**) interconversion is probably limited by the fast radical quenching reactions, leading to comparable amounts of both **10a** and **10b**.

The glucose reactions of **6** indicate that radical anion intermediate $7^{\bullet-}$ had formed and that the system has a poorer source of H-atom donors (compared to the AHQ^{2-} case). Consequently, $7^{\bullet-}$ has sufficient time to cyclize to $9a^{\bullet-}$ and $9b^{\bullet-}$, which presumably interconvert, leading to a predominance of *trans*-**10a** over *cis*-**10b** product (ca. 95:5). The quenching of the radical is slow, allowing *cis*-**10b** to further cyclize to the observed indene products (Scheme III).

At 135 °C in 1 M NaOH, glucose can be deprotonated to give an enediolate dianion, which may add to quinonemethides, as demonstrated by Fullerton and Wilkins,[19] or transfer electrons, via the steps shown in eq 1. Russell



and Lawson[26] have produced glyoxal radical ions similar to that proposed in eq 1. There is analogy between enediolate reactions and AHQ^{2-} reactions, both with regard to adduct formation or electron transfer to quinonemethides (eq 2). The reduction potential of α-dicarbonyl compounds, such as 3-oxocamphor, and anthraquinone are very siimilar.[27]

The fact that cyclization products **10** and **12–14** are observed in low yields after lengthy reactions of **6** in 1 M NaOH indicates that $7^{\bullet-}$ has been formed and that there is not a good H-atom donor source in the system. The electron-transfer agent here could be HO^- ($7 + HO^- \rightarrow 7^{\bullet-} + HO^\bullet$) but is more likely a phenolate ion ($7 + 6^- \rightarrow 7^{\bullet-} + 6^\bullet$).

Electron transfer from the active reagents to the quinonemethide **7** could be (a) an outer sphere process, where a single electron transfer (SET) occurs through space, (b) an inner sphere process, where a bond forms between the active reagent and the α-carbon of QM **7** (i.e., an adduct), followed by homolytic fragmentation of the C_α–reagent bond, or (c) transfer of a hydrogen atom (H•) from the reagent to the carbonyl oxygen of the quinonemethide, followed by deprotonation.

Our data do not allow a clear distincition between the possible modes of electron transfer. Based on reasoning and the reactivity of probe compound **7** with other reagents,[18] we prefer the SET mechanism. The inner sphere case should be retarded by the large steric bulk on the β-carbon of the quinonemethide **7**, possibly preventing bonding of glucose, AHQ^{2-}, or a phenolate ion at the α-carbon. In the other case, hydrogen atom transfer should occur preferentially at C_α, rather than at oxygen, based on the much greater HOMO electron density on C_α.[28] Transfer of H• to C_α would not account for the observed cyclization products.

Finally, could benzyl cations or anions be intermediates in the cyclization reactions? A carbocation can be ruled out based on (1) the precedence for cyclization with an intramolecular double bond to give the more stable secondary, cyclohexyl carbocation, rather than a primary, cyclopentylmethyl carbocation, and (2) cyclization was

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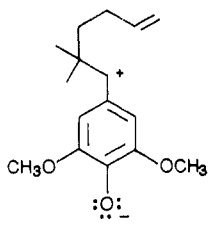
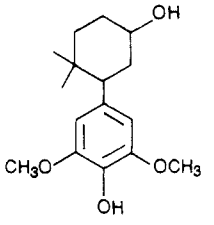
promoted by reducing agents which supply, rather than remove, electrons. Benzylic carbocations might be represented by the resonance form of QM 7 shown below; such a species, "7", may account for the production of minor, incompletely identified products. The MS evidence of minor product **b** (Table I) indicates it is an isomer of **6** and suggests the transposition of the α-OH group of **6** to an ϵ-OH group in a cyclohexane (cyclized) product, such as **15**.

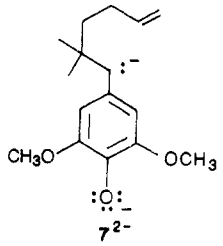


"7"

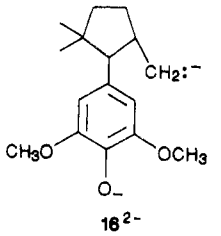


15

Carbanion cyclizations can give rise to cyclopentylmethyl carbanions.[29] Species 7^{2-} could presumably arise by a two electron transfer, either as a single step or two SET steps, between the active reagent and QM 7. The likelihood that 7^{2-} and its conversion to 16^{2-} account for the observed products from **6** is, however, remote.



7^{2-}



16^{2-}

The previous discussion indicates that the changes in observed product distributions with AHQ^{2-} and glucose reflects different rates of quenching of the intermediates. One would hardly expect 7^{2-}, a carbanion, to have any significant lifetime in water at 135 °C before being protonated. Also, the carbanion 16^{2-} would not be expected to form a bond to an electron-rich aryl ring and, therefore, cannot explain the observed indene products.

Conclusions

The reactions of **6** indicate that AHQ^{2-} and glucose transfer electrons to the in situ generated quinonemethide **7**. The transfer could occur by supplying a hydrogen atom, followed by deprotonation, by homolytic cleavage of an adduct or, more likely, by way of an outer sphere (SET) mechanism. Product formations are best rationalized in terms of radical intermediates and radical cyclization (Schemes II and III). Differences in product distributions appear to be related to differences in the rates of radical quenching vs cyclization in the systems studied.

The reactions of **6** provide possible insights into how specific reagents may be promoting pulping reactions.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 700 infrared spectrometer and standardized with polystyrene. A JEOL FX 100 spectrometer was used to obtain the NMR spectra. The mass spectra were obtained with a Hewlett–Packard Model 5985 GC-MS spectrometer using a 6-ft 3% silicone OV-17 on 100/120 Chromosorb W-HP MAOT-350 column.

Syringaldehyde and 4-bromo-1-butene were obtained from Aldrich Chemical Co., Milwaukee, WI, while 1-bromo-4-pentene was obtained from ICN Pharmaceuticals, Inc., K & K Laboratories, Plainview, NY. Ultrapure NaOH was obtained as a 30% solution from Alfa Products, Danvers, MA. Silica gel 60 (70–230-mesh ASTM) was used in all chromatographic separations.

Oxygen-free water was prepared by boiling distilled water for about 30 min, after which nitrogen was dispersed into the water as it cooled to room temperature. After cooling, the water was sealed under nitrogen until needed.

6-Hydroxy-6-(3′,5′-dimethoxy-4′-hydroxyphenyl)-1-hexene (5). To an oven-dried 500-mL three-necked round-bottom flask flushed with nitrogen were added 0.90 g (0.037 g atom) of magnesium turnings and enough anhydrous ether to cover the turnings. Connected to the flask was an oven-dried 250-mL pressure equalizing addition funnel containing a 150-mL anhydrous ether solution of 5.5 g (0.037 g atom) of 5-bromo-1-pentene. A constant flow of nitrogen was maintained through the apparatus as a few drops of 1,2-dibromoethane and about 10 mL of the ether solution were used to initiate the reaction. The remaining ether solution was added to the stirred contents of the flask at a rate that gently refluxed the ether. After the complete addition of the ether, the solution was refluxed for 90 min in a 40 °C water bath. Then about 75 mL of freshly distilled tetrahydrofuran (THF) was added, and the water bath temperature was increased to 70 °C. Syringaldehyde (2.80 g, 0.015 mol) dissolved in 40 mL of THF was dripped into the reaction vessel. An hour after the syringaldehyde addition was complete, the reaction was quenched with 5 mL of water followed by 2 M H_2SO_4. The THF was separated, filtered, dried (anhydrous $MgSO_4$), and evaporated to give a yellow liquid. Analysis of the liquid by ^1H NMR and GC/MS identified the product as the ketone of the title compound.

The ketone was reduced by dissolving the yellow liquid in 50 mL of ethanol and adding dropwise 50 mL of distilled water containing 1.5 g of $NaBH_4$. After stirring overnight, the reaction solution was filtered, quenched with 100 mL of saturated ammonium chloride, and neutralized with 0.5 M H_2SO_4. The aqueous solution was extracted twice with 70 mL of chloroform. The chloroform was combined, dried (anhydrous Na_2SO_4), and evaporated to give a greenish solid. This solid was recrystallized from toluene/35–60 °C petroleum ether to yield 1.70 g of a colorless solid: mp 91–92 °C; IR (mull) cm^{-1} 3150–3600 (PhOH and HCOH), 1615 (CH_2=CH-); ^1H NMR ($CDCl_3$) δ 1.5 (m, 2, C4-H_2), 1.7 (m, 2, C3-H_2), 2.0 (m, 2, C5-H_2), 2.08 (s, 1, -CHO*H*-, exchangeable with D_2O), 3.87 (s, 6, OCH_3), 4.6 (m, 1, -C*H*OH-), 4.9–5.1 (m, 2, CH_2=), 5.56 (s, 1, PhOH, exchangeable with D_2O), 5.56–6.01 (ddt, 1, J = 17, 10, and 6 Hz, =CH-), 6.55 (s, 2, aryl); ^{13}C NMR ($CDCl_3$) ppm 25.1 (t, C4), 33.5 (t, C5), 38.4 (t, C3), 56.1 (q, OCH_3), 74.4 (d, C6), 102.4 (t, CH_2=), 114.3 (d, C2′, C6′), 133.6 (s, C1′), 135.8 (s, C4′), 138.3 (d, =CH-), 146.6 (s, C3′, C5′); MS, m/e (relative intensity) 252 (41, M^+), 183 (100), 155 (47), 140 (30), 123 (95), 95 (57), 77 (32), 41 (53).

Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.67; H, 7.94. Found: C, 66.32; H, 8.36.

5,5-Dimethyl-6-hydroxy-6-(3′,5′-dimethoxy-4′-hydroxyphenyl)-1-hexene (6). Preparation of the Grignard reagent of 5-chloro-5-methyl-1-hexene proved difficult; refluxing ether resulted in the formation of undesired products. These undesired products were prevented by using large volumes of ether at room temperature. However, these conditions prevented the initiation and continuation of the Grignard reaction. To facilitate the reaction, periodic additions of methyl iodide were used to first initiate and then help maintain the reaction. Thus, byproducts from methylmagnesium iodide were formed which had to be subsequently removed.

While in a nitrogen atmosphere, 1.0 g (0.0411 g atom) of magnesium turnings and 150-mL of anhydrous ether were added to an oven-dried 500-mL three-necked round-bottom flask. Added to two oven-dried 250-mL pressure equalizing addition funnels were 50-mL of anhydrous ether with 1.5 g (0.0113 mol) of 5-chloro-5-methyl-1-hexene[30] and 240 mL of anhydrous ether with 2.0 g (0.0141 mol) of methyl iodide, respectively. The glassware was assembled and approximately a fourth of the methyl iodide solution was added to the stirred turnings. When the reaction had started, the dropwise addition of the 5-chloro-5-methyl-1-

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hexene solution was begun. This addition spanned 8–10 h during which the methyl iodide solution was periodically added.

After the reaction solution had stirred overnight, silated syringaldehyde[31] dissolved in anhydrous ether was added dropwise until the brown color associated with the addition was no longer observed. The reaction was quenched with water followed by a small amount of 2 M H_2SO_4. The entire solution was filtered (to remove unreacted Mg) and additional 2 M H_2SO_4 was added. The acid (approximately 1 M) and ether layers were allowed to sit together overnight to remove the silyl protecting group.

The ether layer was separated and extracted with a 1 M NaOH solution to remove the phenolic products. A precipitate formed during this step. The precipitate, which was assumed to be the sodium salt of the desired product, was collected by filtration and redissolved in ether with the help of 0.25 M sulfuric acid. Drying (Na_2SO_4) and evaporation of the ether solution gave a solid, which was recrystallized from hot toluene to give an off-white solid (**6**): mp 111–112.5 °C; IR (mull) cm^{-1} 3150–3600 (OH's) and 1610 (CH_2=CH-); ^1H NMR ($CDCl_3$) δ 0.86 and 0.93 (two s, 3 + 3, *gem*-dimethyls), 1.4 (m, 2, C4-H_2), 1.63 (br s, 1, -CHO*H*-), 2.0 (m, 2, C3-H_2), 3.87 (s, 6, OCH_3), 4.39 (s, 1, -C*H*OH-), 4.8–5.1 (m, 2, CH_2=), 5.46 (s, 1, PhOH), 5.63–5.96 (ddt, 1, J = 17, 10, and 6 Hz, =CH-), 6.54 (s, 2, aryl); shaking the NMR solution with two drops of D_2O removed the hydroxyl proton signals; ^{13}C NMR ($CDCl_3$) ppm 22.9 and 23.0 (two q, *gem*-dimethyls), 28.4 (t, C4), 38.0 (t, C3), 56.2 (q, OCH_3), 81.0 (d, -CHOH-), 104.5 (d, C2′, C6′), 113.6 (t, CH_2=), 132.9 (s, C4′), 133.6 (s, C1′), 139.2 (d, =CH-), 146.0 (s, C3′, C5′); MS, m/e (relative intensity) 280 (7.1, M^+), 183 (100.0), 155 (19.2), 140 (11.8), 123 (32.9), 95 (16.6), 55 (14.9).

Anal. Calcd for $C_{16}H_{24}O_4$: C, 68.57; H, 8.57. Found: C, 68.47; H, 8.51.

Alkaline Reactions of 6. All reaction solutions of **6** were prepared in a nitrogen atmosphere with oxygen-free water and 30% ultrapure NaOH. The reactions were conducted in stainless steel pressure vessels (bombs) of 4-mL capacity. Water and NaOH solution were added to make a 3.5 mL, 1 M NaOH solution. The amount of **6** in each bomb was 0.0196 g (0.020 mol).

The additives used were as follows: AHQ, as an AHQ-diacetate derivative[32] (0.0412 g, 2 molar equiv), glucose (0.0631 g, 5 molar equiv), methyl α- and β-D-glucopyranoside (0.0680 g, 5 molar equiv), Na_2S (0.0109 g, 2 molar equiv), and Na_2SO_3 (0.0441 g, 5 molar equiv). The bombs were sealed and tumbled in a 135 °C oil bath for times ranging from 2 to 18 h. After the desired length of time, the bombs were cooled in water. The contents of the bombs were neutralized with 2 M H_2SO_4 and extracted with chloroform. Analysis of the chloroform solutions was by GC/MS.

Isolation and Characterization of Products. Isolation Procedures. Products **10**, **12**, **13**, and **14** were obtained from the reaction of **6** with 5 molar equiv of glucose at 135 °C in the previously described bombs. This procedure was repeated until 3.3 g of **6** were reacted. The contents of all the bombs were combined, neutralized with 5 M H_2SO_4, and extracted with chloroform. The chloroform was dried (anhydrous Na_2SO_4) and evaporated. The solid was dissolved in a minimum amount of toluene, placed on a silica gel column, and eluted with toluene, with increasing amounts of ethyl acetate added to the toluene. Products **13** and **14** were separated, while products **10** and **12** were eluted together. Solutions containing **10** and **12** were evaporated, and the resulting liquid was placed on another silica gel column. Elution with petroleum ether (35–60 °C) provided satisfactory separation.

Product **8** was obtained from the reaction of 0.8 g of **6** with 2 equiv (1.2 g) of AHQ (prepared by the reduction of anthraquinone with $Na_2S_2O_4$) using a large reaction vessel (described in detail elsewhere[34]) and a temperature of 135 °C. The final reaction solution was neutralized with 5 M H_2SO_4 and extracted with toluene. The toluene was dried (anhydrous Na_2SO_4) and evaporated. The solid was extracted with 35–60 °C petroleum ether (done to remove products from the anthraquinone), which in turn was evaporated to a minimum volume, placed on a silica gel column, and eluted with 35–60 °C petroleum ether. A good separation of **8** was obtained. Spectral data for products **8**, **10**, **12**, **13**, and **14** are presented below and in Table I.

5,5-Dimethyl-6-(3′,5′-dimethoxy-4′-hydroxyphenyl)-1-hexene (8): IR cm^{-1} 1610 (CH=CH_2); ^1H NMR ($CDCl_3$) δ 0.87 (s, 6, CH_3), 1.2–1.4 (m, 2, C4-H_2), 2.0–2.2 (m, 2, C3-H_2), 2.42 (s, 2, C6-H_2), 3.82 (s, 6, OCH_3), 4.7–5.1 (m, 2, CH_2=), 5.48 (br s, 1, OH), 5.50–6.02 (ddt, 1, J = 17, 10, and 6 Hz, =CH-), 6.31 (s, 2, aryl); MS, m/e (relative intensity) 264 (19.8, M^+), 168 (40.6), 167 (100.0).

***trans*-2-(3′,5′-Dimethoxy-4′-hydroxyphenyl)-1,1,3-trimethylcyclopentane (10a)**: ^1H NMR ($CDCl_3$) (*syn* and *anti* designations are relative to the aryl ring) δ 0.65 (s, 3, C1-*syn*-CH_3), 0.93 (d, 3, J = 7Hz, C3-CH_3), 0.97 (s, 3, C1-*anti*-CH_3), 1.3 (m, 1, cyclopentyl H), 1.5–1.65 (m, 2, two cyclopentyl H), 2.0 (m, 1, *syn*-C4- or -C5-H), 2.11 (d, 1, J = 11 Hz, C2-H), 2.35 (m, 1, *syn*-C4- or -C5-H), 3.87 (s, 6, OCH_3), 5.39 (s, 1, OH), 6.35 (s, 2, aryl); MS, m/e (relative intensity) 264 (81.4, M^+), 168 (100.0), 167 (43.1).

Molecular models indicate that (1) the methyl groups on C1 and C3 which are *syn* to the C2-aryl ring are situated in the shielding region of the aryl ring and will therefore be upfield in the ^1H NMR spectrum and (2) cyclopentyl ring protons on the C4 and C5 carbons which are *syn* to the aryl ring are in a deshielded region and will therefore be downfield. The trans assignment to the **10** isolated above is based on the fact that the chemical shift of the C3-methyl (δ 0.93) is similar to the C1-*anti*-methyl (δ 0.97) and not the C1-*syn*-methyl (0.65).

The ^1H NMR spectrum of **10a** contains weak signals attributed to the presence of the *cis*-**10b** isomer. The cis isomer displays a doublet methyl at δ 0.78 (*syn*-C3-methyl), singlet methyl groups at 0.75 and 1.12 (*syn*- and *anti*-C1-methyl, respectively), a doublet benzylic proton at 2.52 (J = 7 Hz), and C4/C5-*syn*-ring proton as multiplets at 1.8 and 2.7.

12,12-Dimethyl-4,6-dimethoxy-5-hydroxytricyclo-[7.3.0.0^{2,7}]-2,4,6-dodecatriene (12): ^1H NMR ($CDCl_3$) δ 0.70 and 1.15 (two s, 3 + 3, *gem*-dimethyls), 0.8–3.2 (several m, C1-H, C3-H_2, C4-H_2, C5-H_1, C_6-H_2), 3.84 and 3.86 (two s, 3 + 3, OCH_3), 5.58 (s, 1, OH), 6.47 (s, 1, aryl); MS, m/e (relative intensity) 262 (100.0, M^+), 206 (20.2), 205 (78.8).

12,12-Dimethyl-5-hydroxy-4-methoxytricyclo[7.3.0.0^{2,7}]-2,4,6-dodecatriene (13): ^1H NMR ($CDCl_3$) δ 0.72 and 1.16 (two s, 3 + 3, *gem*-dimethyls), 0.9–3.2 (several m, C1-H, C3-H_2, C4-H_2, C5-H_1, C6-H_2), 3.85 (s, 3, OCH_3), 5.50 (s, 1, OH), 6.66 and 6.68 (two s, 2, aryl); MS, m/e (relative intensity) 232 (85.7, M^+), 176 (27.0), 175 (100.0), 162 (12.6), 161 (10.3), 147 (12.6).

12,12-Dimethyl-4,6-dimethoxy-5-hydroxytricyclo-[7.3.0.0^{2,7}]-2,4,6-dodecatriene (12): ^1H NMR ($CDCl_3$) δ 0.70 and 1.15 (two s, 3 + 3, *gem*-dimethyls), 0.8–3.2 (several m, C1-H, C3-H_2, C4-H_2, C5-H_1, C_6-H_2), 3.84 and 3.86 (two s, 3 + 3, OCH_3), 5.58 (s, 1, OH), 6.47 (s, 1, aryl); MS, m/e (relative intensity) 262 (100.0, M^+), 206 (20.2), 205 (78.8).

12,12-Dimethyl-5-hydroxy-4-methoxytricyclo[7.3.0.0^{2,7}]-2,4,6-dodecatriene (13): ^1H NMR ($CDCl_3$) δ 0.72 and 1.16 (two s, 3 + 3, *gem*-dimethyls), 0.9–3.2 (several m, C1-H, C3-H_2, C4-H_2, C5-H_1, C6-H_2), 3.85 (s, 3, OCH_3), 5.50 (s, 1, OH), 6.66 and 6.68 (two s, 2, aryl); MS, m/e (relative intensity) 232 (85.7, M^+), 176 (27.0), 175 (100.0), 162 (12.6), 161 (10.3), 147 (12.6).

12,12-Dimethyl-5-hydroxy-6-methoxytricyclo[7.3.0.0^{2,7}]-2,4,6-dodecatriene (14): ^1H NMR ($CDCl_3$) δ 0.70 and 1.14 (two s, 3 + 3, *gem*-dimethyls), 0.9–3.3 (several m, C1-H, C3-H_2, C4-H_2, C5-H_2), 3.85 (s, 3, OCH_3), 5.50 (s, 1, OH), 6.76 (s, 2, aryl); MS, m/e (relative intensity) 232 (100.0, M^+), 176 (30.2), 175 (91.7), 162 (14.3), 131 (11.7), 115 (13.8).

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Supplementary Material Available: GC traces for the data presented in Table I (1 page). Ordering information is given on any current masthead page.

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