Products from the Acid-Catalyzed Reaction of Cyclic Monoterpenes and Phenol

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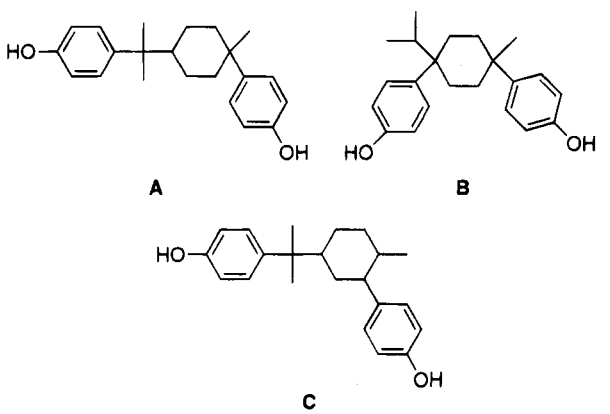
Nine phenol-containing products from the acid-catalyzed reaction of phenol and γ-terpinene were isolated and identified. A combination of X-ray crystallographic and spectroscopic techniques was used to assign the structures of the three *p,p*-bisphenols, two *o,p*-bisphenols, two bicyclic monophenols, and two bicyclic phenyl ethers. Several of the individual reaction products interconverted under acid-catalyzed conditions. The same nine products were formed using 3-carene, α-pinene, limonene, or sabinene in place of γ-terpinene, although the relative concentrations of these products varied depending upon the starting monoterpene's structure. A mechanism is proposed which accounts for the products' structures and reactivities.

Introduction

The product mixture from the acid-catalyzed reaction of phenol and cyclic monoterpenes has found wide use in applications[1] such as phenolic resin insulators and coatings, thermal transfer receptor sheets, hot melt adhesives, and epoxy resins. Typically, these applications involve a multistep process where the crude reaction product is cured or cross-linked by further reaction with another polyolefin, formaldehyde, epichlorohydrin, or a transition metal salt. Despite these uses, and the more general interest in the addition reactions of electrophiles to cyclic monoterpenes,[2] literature describing the isolation and characterization of the product mixture's constituents is fraught with inconclusive or contradictory results.

An early study of the reaction of limonene and phenol states that a mixture of products is formed but does not pursue further characterization.[3] In ensuing years, other reports have described the product mixture as containing polymeric hydrocarbon resins,[4] bicyclic ethers,[5] monophenols,[6] and/or bisphenols.[7] Differences in reaction conditions, including monoterpene structure, acid catalyst type, terpene–phenol stoichiometry, and reaction temperature do not reconcile the differences in reported product distributions.

Literature that mentions the presence of bisphenols in the product mixture illustrates the existing confusion. Roughly half of the references claim[7a–e] that the reaction gives a single product, **A** ("2,8-menthanebisphenol"), in yields as high as 95%. Other reports state[7f–k] that mixtures of bisphenols and other compounds (ethers, monophenols, etc.) are obtained from such a reaction. Even among these most detailed reports, there are inconsistencies. Different structures are proposed (primarily mixtures of **A** and bisphenols **B** and/or **C**), no assignments of relative configurations of the cyclohexane



ring substituents are made, and characterization data are not present or are different from report to report. In summary, a conclusive structure assignment of the phenol-containing products from this reaction has yet to appear.

Herein, we report the isolation and characterization of the major phenol-containing products from the reaction

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(1) Gozenbach, C. T.; Jordan, M. A.; Yunick, R. P. In *Encylopedia Of Polymer Science and Technology*; Mark, H., Gaylord, N. G., Eds.; Wiley-Interscience: New York, 1970; Vol. 13, pp 575–595.

(2) Thomas, A. F. In *Terpenoids And Steroids*; Overton, K. H., Ed.; The Chemical Society: London; 1974; Vol 4., pp 25–35.

(3) Schrauth, W.; Quasebarth, K. *Ber. Dtsch. Chem. Ges.* **1924**, *57*, 854.

(4) Panda, S. P.; Kulkarni, S. G. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 6549.

(5) (a) Sedel'nikov, A. I.; Tikhonova, T. S.; Polyakova, N. P.; Larionov, V. P. *Gidroliz. Lesokhim. Promst.* **1985**, 12; *Chem. Abstr.* **1986**, *104*, 19686r. (b) Laan, J. A. M.; Giesen, F. L. L.; Ward, J. P. *Chem. Ind. (London)* **1989**, 354. (c) Rodionov, V. N.; Kozlikovskii, Y. B.; Andrushchenko, V. A. *Zh. Org. Khim.* **1991**, *27*, 2627; *Chem. Abstr.* **1976**, *117*, 48929w.

(6) (a) Verghese, J. *Flavour Ind.* **1972**, 252. (b) Moskvichev, V. I.; Kheifits, L. A. *Zh. Org. Khim.* **1973**, *9*, 2256; *Chem. Abstr.* **1974**, *80*, 83267t. (c) Lahourcade, B.; Hirigoyen, C.; Jouillie, M.; Maillard, G.; Lakah, L.; Warolin, C. Ger. Patent 2,600,473, 1976; *Chem. Abstr.* **1976**, *85*, 177688m.

(7) (a) Bader, A. R. U.S. Patent 2,811,564, 1957. (b) Verghese, J. *Perfum. Essent. Oil Rec.* **1969**, *60*, 271. (c) Gao, N.; Zhu, Y.; Qian, J. *Shanghai Keji Daxue Xuebao* **1985**, 77; *Chem. Abstr.* **1984**, *101*, 193757n. (d) Sadykhov, S. G.; Kaliyan, L. Y.; Soldatova, V. A. *Azerb. Neft. Khoz.* **1984**, 46; *Chem. Abstr.* **1984**, *101*, 191233q. (e) Tokita, M.; Yasuda, K. Japan Patent 02,214,691, 1989; *Chem. Abstr.* **1991**, *114*, 174987. (f) Moskvichev, V. I.; Kheifits, L. A. *Zh. Vses. Khim. Ova.* **1975**, *20*, 479; *Chem. Abstr.* **1976**, *84*, 31251w. (g) Wakabayashi, S.; Matsubara, Y. *Nippon Kagaku Zasshi* **1959**, *80*, 1179. (h) Watanabe, Y. *Kogyo Kagaku Zasshi* **1960**, *63*, 154. (i) Watanabe, Y. *Kogyo Kagaku Zasshi* **1961**, *64*, 1442. (j) Belg. Patent 670,691 1966; *Chem. Abstr.* **1966**, *65*, 7316c. (k) Brit. Patent 1,103,305 1968; *Chem. Abstr.* **1968**, *68*, 78768e.

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Table 1. Product Distribution from the Reactions of Phenol and Cyclic Monoterpenes

	product area (%)[a]									
terpene	1	2	3	4	5	6	7	8	9	others
γ-terpinene	41.6	16.9	6.2	1.6	2.0	5.7	5.2	2.8	5.0	13.0
3-carene	39.8	13.9	4.5	0.7	1.7	9.4	4.2	2.7	6.0	17.1
sabinene	35.6	21.0	11.5	0.8	0.3	8.1	5.7	3.5	2.8	10.7
limonene	33.6	24.8	11.2	1.1	1.2	4.8	4.9	4.4	3.2	10.8
α-pinene	26.9	18.4	6.9	1.2	1.1	4.7	4.9	3.8	3.1	29.0

[a] Determined by integration of HPLC signals from UV detector (254 nm).

of phenol and a variety of cyclic monoterpenes and propose a mechanism by which they are formed.

Results and Discussion

Isolation and Identification of Products 1–9. The first phase of this investigation involved the isolation and identification of the phenol-containing products from the reaction of phenol and a representative cyclic monoterpene. As such, we analyzed the products from the reaction of γ-terpinene and 7 equiv of phenol catalyzed by acidic ion-exchange resin (Amberlite 118, 100 °C, 5 h). The reaction gave a complex mixture of products. The distribution of phenol-containing species was determined by HPLC chromatographic analysis, and these results are summarized in Table 1 for the nine compounds isolated and identified in this study.

Products **1–9** were purified by a combination of fractional crystallization and flash column chromatography. The structures of these compounds were assigned in the following manner.

X-ray crystallographic analysis was used to conclusively determine the structures of bisphenols **1** and **2**. For this purpose, the bisphenols were converted to their respective diacetates (acetic anhydride/H_2SO_4). Crystals with sufficient quality for structure analysis could then be obtained by recrystallization from methanol. Cleavage of a portion of the diacetates (K_2CO_3/methanol) gave back bisphenols **1** and **2**, indicating that no structural rearrangement (i.e., epimerization) occurred during diacetate formation.

An X-ray crystallographic experiment[8] on the diacetate established the structure of bisphenol **1** to be (1α,3α,4β)-4-[1-[3-(4-hydroxyphenyl)-4-methylcyclohexyl]1-methylethyl]phenol (see Figure 1). In this structure, one phenol group has added directly to the terpene cyclohexane ring, while the second phenol group has bonded to the exocyclic isopropyl position. This substitution pattern indicates that phenol alkylation occurs with one secondary and one tertiary cation, respectively. The three cyclohexane ring substituents all occupy equatorial configurations which minimize their steric interactions and which accentuate the linear structure, or aspect ratio, of this bisphenol. The carbon connectivity determined for **1** had been previously proposed to be a product from monoterpene–phenol reactions (i.e., structure **C**). However, this is the first assignment of the relative stereochemistry of this product.

Crystallographic analysis of the second diacetate provided the structure of bisphenol **2**, namely (1α,3α,4β)-4,4′-[1-methyl-4-(1-methylethyl)-1,3-cyclohexandiyl]bisphenol (Figure 1).[8] Again, one phenol is attached at a quarternary carbon while the second is bonded to a tertiary carbon. In contrast to bisphenol **1**, however, both phenol groups are bonded directly to the terpene cyclohexane ring in bisphenol **2**. The two phenol rings and the isopropyl substituent are attached in equatorial positions, while the smaller quarternary methyl substituent is in an axial position. Steric proximity between the 3-phenol and 4-isopropyl substituents is reflected by the atomic planes of these two groups being nearly parallel to each other and perpendicular to the cyclohexane ring plane. The carbon skeleton found for **2** has not previously been reported to arise from terpene–phenol reactions. It is, however, interesting to note that bisphenol **2** has been proposed[9] as the structure of a natural product isolated from a North Atlantic marine hydra.

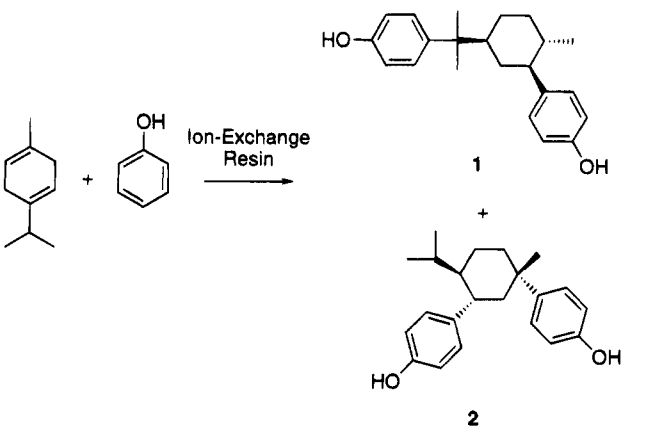


Figure 1. Predominant products from the acid-catalyzed reaction of phenol and γ-terpinene.

Minor components from the reaction mixture were purified by flashcolumn chromatography. The structures of several other bisphenol products were assigned by a combination of spectroscopic and chemical means. For example, compound **3** was found to be an epimer of bisphenol **2**, where the configurations of the phenol and methyl groups bonded to cyclohexane ring C-1 were switched. This assignment of structure was supported by similarities between the ^1H and ^{13}C NMR spectra. For example, both compounds exhibited signals characteristic of two nonequivalent *p*-substituted phenol groups and the terpene methyl group bonded to a quarternary carbon. Furthermore, under prolonged exposure to acidic conditions (100°C, 20 equiv of phenol, Amberlite 118), bisphenols **2** and **3** reacted to give the same product mixture (Figure 2). Starting with either pure **2** or pure **3**, an equilibrium mixture containing 49% **2** and 51% **3** was obtained. The half lives of these reactions were 5 days. Apparently, under acidic conditions either bisphenol reversibly loses 1 equiv of phenol to give a common, tertiary cation intermediate. This intermediate then adds phenol to either face of the terpene cyclohexane ring, resulting in the mixture of bisphenols **2** and **3**.

Bisphenol **4** is another isomer of bisphenol **2** where one phenol group attached to the terpene cyclohexane ring is bonded in the o-position rather than the *p*-position. NMR spectroscopic analysis clearly indicated that **4** contained one *o*-substituted phenol group and one *p*-substituted phenol group (10 signals in the ^{13}C NMR spectrum and an overlapping AB doublet of doublets and

(8) The authors have deposited the atomic coordinates, bond distances, and bond angles for the X-ray structures of the diacetates of **1** and **2** at the Cambridge Crystallographic Data Center. These data can be obtained, on request, from the Director, Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1E2, U.K.

(9) Pathirana, C.; Anderson, R. J.; Wright, J. C. L. *Tetrahedron Lett.* **1989**, *30*, 1487.

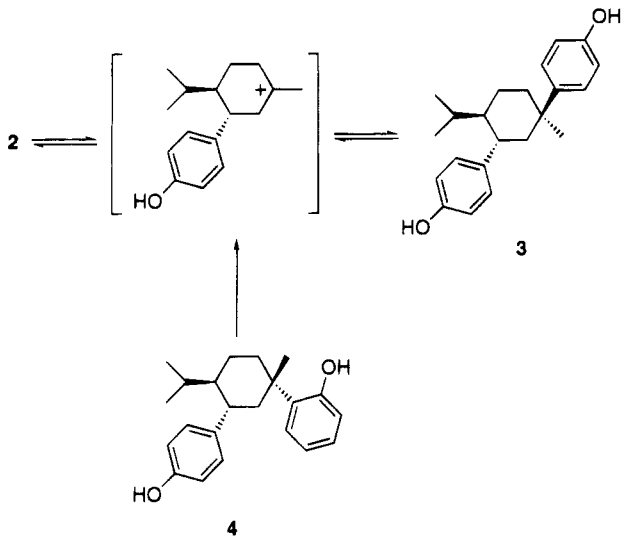


Figure 2. Acid-catalyzed interconversion of bisphenols **2**, **3**, and **4**.

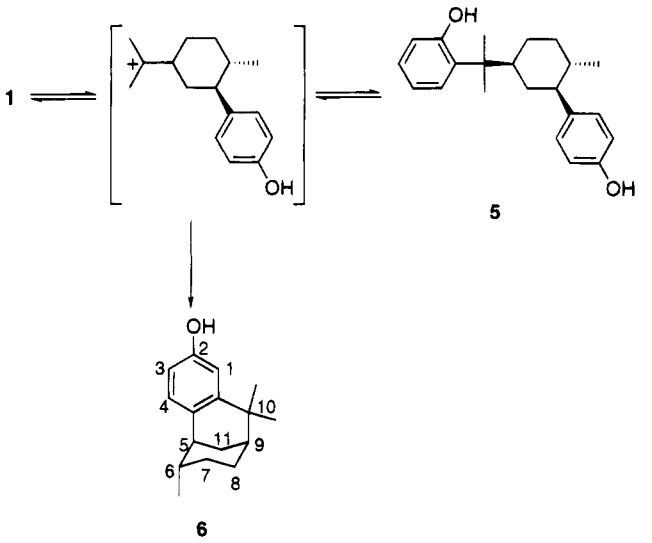


Figure 3. Formation of phenol **6** from bisphenol **1** or **5**.

1,2-disubstituted aromatic pattern in the ^{1}H NMR). A ^{1}H NMR NOESY experiment established the position of the *o*- and *p*-bonded phenol groups. This confirmed the spatial proximity between the 3-H of the *o*-substituted phenol group and the terpene methyl group, while the 3-H and 5-H signals of the *p*-substituted phenol group correlated with the terpene isopropyl methyl signals. Finally, when pure *o*,*p*-bisphenol **4** was heated with excess phenol under acidic conditions (20 equiv of phenol, 100 °C, Amberlite 118), it was cleanly converted to a mixture of bisphenols **2** and **3**. Within 24 h, **4** was consumed completely and a 3/1 mixture of bisphenols **2/3** appeared, similar to the ratio present in the crude γ-terpinene/phenol product mixture. However, upon being heated further, this kinetic product was transformed to the thermodynamic, near-equal mixture of **2** and **3** described above (Figure 2). Both the reactivity and spectroscopic properties of **4** indicated that the *o*-phenol group was substituted on the terpene cyclohexane ring at the quarternary carbon.

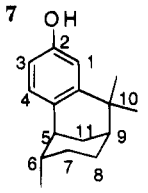
A similar line of reasoning was used to assign the structure of **5** as an *o*,*p*-isomer of *p*,*p*-bisphenol **1**. Once again, bisphenol **5** had the spectral attributes characteristic of both *o*- and *p*-substituted phenol subunits. In addition, a NOESY ^{1}H NMR experiment indicated spatial proximity between the *o*-phenol group and the geminal isopropylidene methyl groups and between the *p*-phenol and the single methyl group bonded to the cyclohexane ring. Finally, bisphenols **5** and **1** were both converted under forcing conditions to a common product, monophenol **6** (Figure 3). Loss of either a *p*-phenol group from **1** or the *o*-phenol group from **5** generated an exocyclic, tertiary cation intermediate. Intramolecular cyclization of this intermediate then gave the methanobenzocyclooctene skeleton of **6**. Monophenol **6** was found to be present, at low concentration, in the crude γ-terpinene/phenol product mixture as well. Therefore, extensive spectroscopic analysis was used to conclusively assign the structure of **6**.

First, a parent ion at $m/z = 230$ in the mass spectrum indicated that compound **6** contained one phenol and one terpene subunit. The substitution pattern of the phenol group was readily assigned on the basis of chemical shifts and carbon multiplicities, by DEPT experiments, of the aromatic ^{13}C NMR signals. The chemical shifts of the three quaternary and three methine carbons were characteristic of a 3,4-disubstituted phenol. As such, the carbon bearing the phenolic OH was observed at 153.4 ppm, while the two protonated carbons ortho to the phenolic OH were assigned at 112.4 and 112.6 ppm. The more shielded of the remaining unprotonated aromatic carbon resonances (134.8 ppm) was assigned to the carbon para to the phenol group. This left the *m*-positions occupied by one hydrogen (129.1 ppm) and one alkyl substituent (148.1 ppm).

While the aliphatic regions of both the carbon and proton NMR spectra of **6** were more complex, a combination of 1-D and 2-D experiments provided the information which made a complete structure assignment possible. A ^{13}C NMR DEPT experiment ascribed the ten aliphatic signals to three methyl, three methylene, three methine, and one quarternary carbon. Taken together, the ^{13}C NMR and mass spectral results indicated that the phenol group must have been fused to a bicyclic aliphatic portion. Two methyl singlets in the ^{1}H NMR (1.30 and 1.21 ppm) showed that two of the methyl carbons must be bonded to the quarternary carbon. As in bisphenol **1**, this quarternary carbon forms a bridge between the phenol ring and the terpene cyclohexane ring. The third methyl group gave a doublet in the ^{1}H NMR (1.16 ppm, $J = 7.2$ Hz), indicating it was bonded to a methine carbon. The remaining six methylene and methine carbons, therefore, constituted the terpene-derived cyclohexane ring.

Completion of structure determination of **6** required the assignment of the position and relative stereochemistry of the three cyclohexane substituents. First, HETCOR and ^{1}H decoupling experiments found that two methylene groups were neighbors, while the third was isolated from these two. The protons on C-7 and C-8 (using the numbering scheme for a methanobenzocyclooctene ring system shown in Figure 3) gave large mutual axial−axial coupling, while neither exhibited a large coupling to signals arising from the C-11 methylene group. The "1,2,4" pattern of methylene groups in the cyclohexane ring means that each of the methine groups was bonded to at least one methylene group. Inspection of the coupling patterns of the three methine protons found that each exhibited only small ($J \leq 5.0$ Hz) coupling, which would come from axial−equatorial and longer range (i.e., "w") coupling. The absence of any large coupling for the methine protons indicated no axial−axial

Table 2. Experimental and Calculated Proton Chemical Shift Differences for Cyclohexane Ring Protons of 6 and



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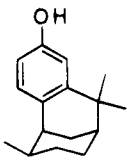

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	chemical shift (δ)		δ 6 − δ 7	
proton	6	7	exp	calc
H-5	2.53	2.62	−0.09	−0.17
H-6	1.73	1.75	−0.02	0.15
$H\text{-}7_{ax}$	1.28	0.68	0.60	0.60
$H\text{-}7_{eq}$	0.88	1.13	−0.25	−0.17
$H\text{-}8_{ax}$	1.67	1.48	0.19	0.24
$H\text{-}8_{eq}$	1.87	1.97	−0.10	−0.26
H-9	1.58	1.61	−0.03	0.00
$H\text{-}11_{ax}$	1.86	2.18	−0.32	−0.26

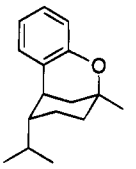
coupling, and therefore, the protons must each occupy the equatorial position on their carbons. Consequently, all three cyclohexane substituents were in the axial positions, as shown for **6**. As a confirmation of this assignment, ^{1}H NMR COSY experiments showed the long-range, w coupling between the equatorial proton on C-6 and C-8 and C-11 and between those on C-5 and C-7 and C-9 that would be expected for the rigid bicyclic structure.

The spectroscopically derived structure of **6** was also supported by consideration of the structure of its precursor, bisphenol **1**. The methyl and isopropylidene substituents on **1** occupy trans 1,4-positions on the cyclohexane ring. Through the steps of losing one phenol group and subsequent cyclization of the cation intermediate, this trans relationship should be maintained. In fact, product **6** does exhibit this same relative configuration, with the axial substituents at C-6 and C-9 being trans to each other.

Chromatography of the crude γ-terpinene/phenol product mixture yielded another monophenol, **7**, which exhibited properties which were in many respects similar to those of **6**. Both compounds had the same molecular mass and the same number and types of carbons, as assigned by ^{13}C NMR. The chemical shifts for signals in the ^{13}C and ^{1}H NMRs of **6** and **7** were, however, decidedly different. Therefore, **7** was analyzed by 1-D and 2-D NMR in a manner similar to that described above for **6**. The structure of **7** derived from these experiments differed from **6** only in the configuration of the C-6 methyl group, which is equatorial in **7** as opposed to axial in **6**.

Despite the other larger substituents common to structures **6** and **7**, differences in the ^{1}H and ^{13}C NMR chemical shifts of the cyclohexane atoms can be explained reasonably well by the difference in methyl group orientation. For example, in Table 2 the differences in chemical shifts for the protons of the cyclohexane rings of **6** and **7** are listed. These values are compared with analogous chemical shift differences calculated between axial and equatorial methylcyclohexanes.[10] Agreement between the calculated and experimental shift differences is excellent, further validating the assignments of structures **6** and **7**.

Finally, two cyclic ethers, **8** and **9**, were isolated. Compounds of this type have been previously reported[11] to be the major products from the condensation reactions of terpenes and phenols which contain substituents in the *p*-position, but this is the first report of this class of products from the reaction of unsubstituted phenol. The



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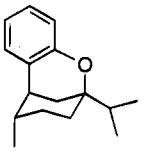

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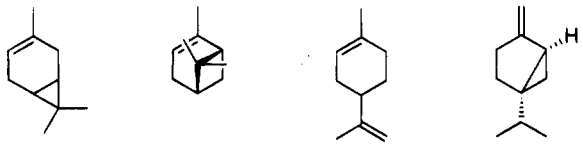
absence of an O−H stretch signal in the infrared spectra of **8** and **9** suggested that they were phenyl ethers. Additional evidence for this came from their ^{13}C NMR spectra, both of which had high-field signals characteristic of quarternary aliphatic ether carbons (74.6 ppm in **8**, 79.2 ppm in **9**). Furthermore, the ^{1}H NMR spectra of **8** and **9** both had aromatic signals consistent with a 1,2-disubstitution pattern as well as strong absorption bands at 750 cm^{-1} in the infrared spectra of the two ethers.

Structures **8** and **9** were easily differentiated by comparing the respective ^{1}H NMR coupling patterns of the terpene methyl and isopropyl substituents. The methyl signal in **8** was a singlet at 1.34 ppm, indicating it was attached to a quarternary carbon. In contrast, the methyl signals for **9** was a doublet (1.13 ppm, J = 7.2 Hz), showing that it was bonded to a tertiary carbon. The axial configurations of the isopropyl group in **8** and the methyl group in **9** were assigned from the coupling patterns of the tertiary (C-4) proton signals. In both cases, the multiplets contained no splitting with J > 8.0 Hz, signifying the absence on any H_{ax}−H_{ax} coupling.

Effect of Monoterpene Structure on Product Distribution. We next explored the relationship between starting cyclic monoterpene structure and the distribution of the phenol-containing reaction products. Terpenes investigated besides γ-terpinene included 3-carene, sabinene, limonene, and α-pinene. All other reaction parameters were kept the same as those used for the



3-Carene α-Pinene Limonene Sabinene

γ-terpinene reaction (7 equiv of phenol, 100 °C, 20 h, acidic ion-exchange resin). The results from these experiments are summarized in Table 1.

Each reaction, regardless of starting monoterpene structure, gave a mixture of products that included compounds **1**−**9**. In all cases bisphenols **1** and **2** were the predominant products, with the two accounting for 45−60% of the total product. While these reaction conditions consistently favored formation of **1** over **2**, there was some variation in the relative amounts of these two major products. Starting from 3-carene, **1** was favored over **2** by a 3:1 margin, while using α-pinene as the starting

(10) Pretsch, E.; Seibl, J.; Simon, W.; Clerc, T. *Spectral Data For Structure Determination Of Organic Compounds*, 2nd ed.; Springer-Verlag: New York, 1989.

(11) (a) Stevens, K. L.; Jurd, L.; Manners, G. *Tetrahedron* **1974**, *30*, 2075. (b) Pottier, E.; Savidan, L. *Bull. Soc. Chim. Fr.* **1977**, 557. (c) Pottier, E. *Bull. Soc. Chim. Fr.* **1981**, 335.

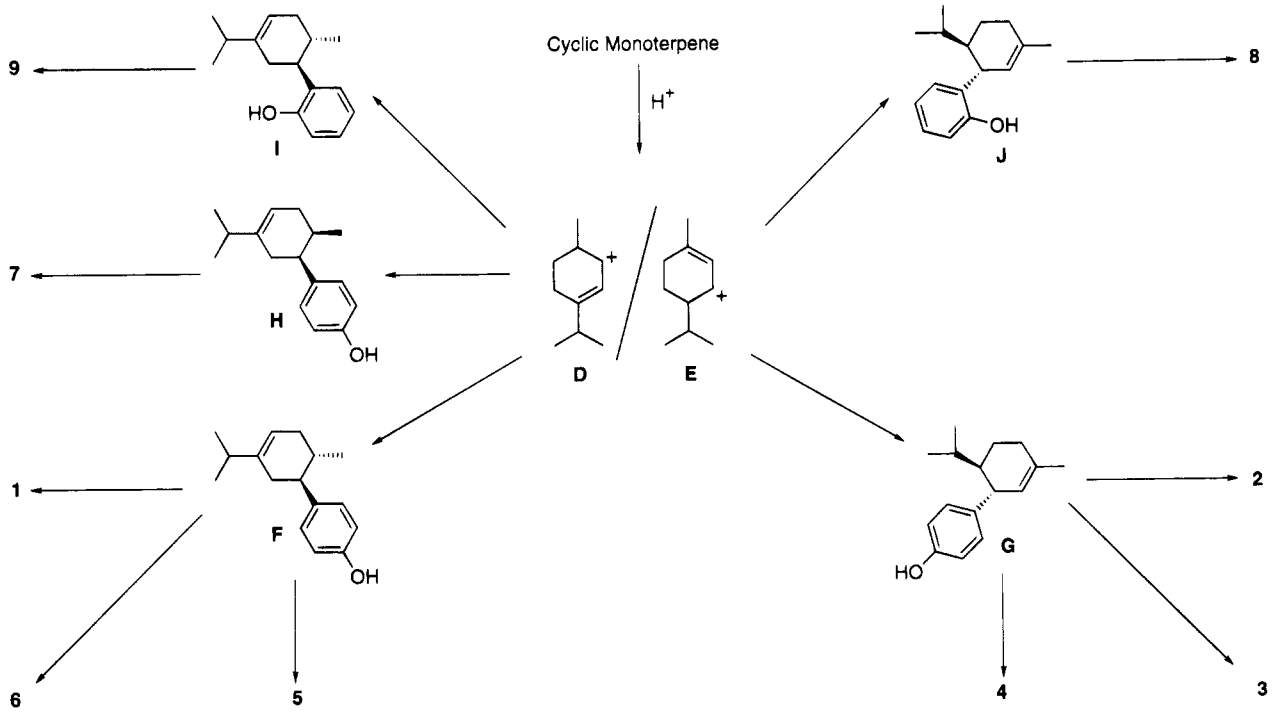


Figure 4. Mechanism of formation for products **1**–**9** from phenol and a cyclic monoterpene.

material gave a mixture where **1** was favored by a ratio of only 1.5:1. The distribution of minor products **3**–**9** was also somewhat dependent upon the starting monoterpene structures. These effects are described later in relation to the proposed reaction mechanism.

In addition to products **1**–**9**, all reactions mixtures contained other minor, as yet unidentified, phenol-containing products. Starting from most monoterpenes, the sum of these other products ranged between 10 and 15 % of the total, with no individual component present at a concentration greater than 3 %. An exception was the reaction of phenol with α-pinene, where the sum of these other products was a significant (29%) fraction of the total product. Preliminary analysis indicated that the α-pinene reaction gave higher than normal levels of 1:1 phenol:terpene adducts, the structures of which are currently being investigated. Finally, it should be noted that, in addition to these phenol-containing species, approximately 10 wt % of the product from each reaction was a hydrocarbon resin formed by competing acid-catalyzed self-oligomerization of the cyclic monoterpene.

Mechanism of Product Formation. A mechanism can be proposed which agrees with all the observed product structure and reactivity data obtained for the acid-catalyzed reaction of cyclic monoterpenes and phenol. In the first step of this mechanism, protonation of the cyclic monoterpene gives a pair of allylic cations, defined as **D** and **E** in Figure 4. The observation that the same products, **1**–**9**, arise from all starting terpene structures strongly suggests common intermediates in the mechanistic pathways. In addition, facile acid-catalyzed interconversion between cyclic monoterpenes is well documented.[12] Formation of at least a pair of protonated intermediates agrees with the earlier conclusions that a number of species are at equilibrium under acidic conditions, reflecting a fine balance of steric and electronic factors which stabilize the different cations.

The initially generated cations **D** and **E** react with phenol to give products **1** - **9** by pathways illustrated in Figure 4. *p*-Alkylation of phenol is the preferred reaction for the pair of cyclohexyl cations. In both cases, alkylation trans to the neighboring cyclohexyl alkyl groups is sterically preferred, giving intermediates **F** and **G**, respectively. Protonation of these monophenol intermediates following, in the case of **F**, isomerization to the exocyclic isopropylidene position gives a pair of tertiary cations which react further to give several of the observed final products. *p*-Alkylation by a second equivalent of phenol is, once again, the favored reaction. This gives as the two predominant products bisphenols **1** and **2**.

The relationships between intermediates **F** and **G** and secondary products **3**–**6** were uncovered by the previously described acid-catalyzed reactions of these purified compounds with phenol, illustrated in Figures 2 and 3. To reiterate, bisphenols **4** and **5** arise from *o*-alkylation of the two intermediates by phenol. Intramolecular cyclization of the cation derived from **F** to give monophenol has been shown to be a thermodynamic sink for the **F**-based branch of the mechanism. Observation of small amounts of **6** in the crude reaction mixtures reflects either a minor kinetically-based concentration or possibly some equilibration of products under the reaction conditions. Finally, as has been described, bisphenol **3** is formed by alkylation of the "reverse" face of cation derived from intermediate **G**.

Returning again to the reactions of cations **D** and **E**, cis-alkylation is disfavored due to steric hindrance of the approaching phenol. However, in the case of cation **D**, the methyl substituent is sufficiently compact so that a small amount of cis-alkylation may occur to give intermediate **H**. Protonation/isomerization of **H** gives a tertiary exocyclic isopropylidene cation which intramolecularly cyclizes to give monophenol **7**. Steric hindrance by the isopropyl substituent on cation **E** is expected to

(12) (a) Bates, R. B.; Caldwell, E. S.; Klein, H. P. *J. Org. Chem.* **1969**, *34*, 2615. (b) McCormick, J. P.; Barton, D. L. *Tetrahedron* **1978**, *34*, 325. (c) Muneyuki, R.; Yoshimura, Y.; Tori, K.; Terui, Y.; Shoolery, J. N. *J. Org. Chem.* **1988**, *53*, 358.

be more severe, so that the ratio of cis- to trans-alkylation would be much smaller from **E** than from **D**. This might explain why the analogous monophenol which would come from **E** was not observed in this study.

Finally, *o*-alkylation of cations **D** and **E** by phenol, adding trans to the neighboring cyclohexyl alkyl substituents, gives intermediates **I** and **J**, respectively. Protonation of these intermediates generates tertiary cations which intramolecularly O-alkylate the phenoxy groups to give bicyclic ethers **8** and **9**.

That the complex mixture of products from the reaction of phenol and cyclic monoterpenes arises from initial formation of a pair of cations followed by a small number of simple, individual steps accounts for a number of observations concerning the product distributions. First, branching of products from these two primary intermediates explains the symmetrical, pairwise occurrence of most of the products (i.e., *p,p*-bisphenols **1** and **2**, *o,p*-bisphenols **4** and **5**, and bicyclic ethers **8** and **9**). In addition, the observed concentration dependence of minor products **3**–**9** on terpene structure, reported in Table 1, can be traced to the initially formed ratio of cations **D** and **E**. For example, reactions that favor formation of **1** over **2**, as from 3-carene, also give higher ratios of **9/8** (6.0/2.7) and **5/4** (1.7/0.7). By contrast, reactions which give a higher concentration of **2** relative to **1**, as from α-pinene, also produce more **8/9** (2.8/3.1) and more **4/5** (1.2/1.1). That there is not a stronger dependence of product distribution on starting terpene structure may reflect that the ion-exchange resin catalyzed conditions (high temperature, low acid concentration) favor an equilibration of the cations **D** and **E** prior to product formation. Therefore, understanding the mechanism of product formation accounts not only for the observed product structures but also, to a large extent, for the distribution of product concentrations.

Conclusions

The acid-catalyzed reaction between phenol and cyclic monoterpenes has been investigated in detail. The two major products from the reaction were isolated and found, using X-ray crystallographic techniques, to be *p,p*-bisphenols (bisphenols **1** and **2**). Several of the minor products from the reaction were also isolated, and their structures were assigned, on the basis of NMR spectral analysis and chemical reactivity, to be an isomeric *p,p*-bisphenol, two *o,p*-bisphenols, two bicyclic phenols, and a pair of isomeric bicyclic phenyl ethers. Two bisphenols, **A** and **B**, that have been frequently reported to be products from the reactions of phenol and cyclic monoterpenes were not observed during this investigation. Acid-catalyzed conditions were found to interconvert several of the individual reaction products.

The effects of varying the cyclic monoterpene structure on the product distribution were studied. The same products were identified to be present from all five terpene starting materials investigated. However, the concentrations of these products were somewhat dependent upon the terpene structure. Using the amassed structure and reactivity data, a mechanism for product formation is proposed.

Studies directed at determining the structures of other minor products from the terpene–phenol reactions, as well as controlling the selectivity in product formation, are being pursued.

Experimental Section

General. 1-D NMR experiments were carried out on a spectrometer operating at 300 MHz for ^{1}H and at 75.4 MHz for ^{13}C, while 2-D experiments were performed on an instrument operating at 500 MHz for ^{1}H and at 125.8 MHz for ^{13}C. Signals in the ^{13}C NMR spectra were assigned using DEPT experiments. HPLC analyses were performed using a ternary pump system with a water/acetonitrile/methanol gradient program (20 m, 90/9/1 to 50/45/5 ramp, 1.5 mL/flow rate) and a C-18 reverse phase column. Melting points were measured on a capillary apparatus and are not corrected.

Synthesis and Purification of Products 1–9. A solution of phenol (2000 g, 21.2 mol), γ-terpinene (424.5 g, 3.11 mol), and acidic ion exchange resin (200.0 g, Amberlite 118 sulfonated polystyrene–divinyl gel, with 4.94 mequiv of H^+/g of resin) was stirred at 100 °C for 20 h. Analysis by HPLC indicated a product composition as shown in Table 1. The mixture was filtered through a glass funnel to remove the ion-exchange resin beads. Phenol was distilled from the filtrates at reduced pressure (70 °C, 1 Torr). Chloroform (600 mL) was added to the still warm (ca. 50 °C) viscous brown distillation residue. After the residue was cooled to ambient temperature over 10 h, a tan crystalline solid formed. Crude **1** was isolated by filtration (420 g). Recrystallization of the tan solid from chlorobenzene gave pure **1** as small feathery white crystals (290 g). The filtrates were concentrated under vacuum and, upon sitting, deposited a second white solid which was collected by filtration. HPLC analysis indicated a 30/70 mixture of bisphenols **1** and **2**. Recrystallization from isopropyl alcohol gave **2** (28.9 g) as white prisms. Minor products **3**–**9** were isolated from the resulting filtrates by repeated flash column chromatography using silica gel and hexane/ethyl acetate solvent systems (gradients from 0 to 25% of ethyl acetate).

(1α,3α,4β)-4-[1-[3-(4-Hydroxyphenyl)-4-methylcyclohexyl]-1-methylethyl]phenol (1): mp 118.0–121.0 °C; ^{1}H NMR (acetonitrile-d_3) δ 7.14 (d, 2H, J = 8.7 Hz), 6.92 (d, 2H, 8.4 Hz), 6.70 (m, 4H), 2.28 (m, 1H), 1.94 (m, 1H), 1.80 (m, 1H), 1.60 (m, 2H), 1.42 (m, 2H), 1.22 (s, 3H), 1.20 (s, 3H), 1.17–1.03 (m, 2H), 0.58 (d, 3H, J = 6.5 Hz); ^{13}C NMR (acetone-d_6) δ 156.3 (C), 155.7 (C), 141.5 (C), 138.3 (C), 129.0 (CH), 127.8 (CH), 115.8 (CH), 115.4 (CH), 52.6 (CH), 50.2 (CH), 40.0 (C), 38.6 (CH), 37.9 (CH_2), 36.7 (CH_2), 28.5 (CH_2), 26.1 (CH_3), 25.8 (CH_3), 20.7 (CH_3); FD MS m/z 324 (M^+).

(1α,3α,4β)-4,4′-[1-Methyl-4-(1-methylethyl)-1,3-cyclohexanediyl]bisphenol (2): mp 123.0–125.5 °C; 1H NMR (acetone-d_6) δ 8.06 (s, 1H), 8.03 (s, 1H), 7.21 (d, 2H, J = 8.7 Hz), 7.07 (d, 2H, J = 8.4 Hz), 6.77 (d, 2H, J = 8.0 Hz), 6.75 (d, 2H, J = 8.6 Hz), 2.73 (m, 1H), 1.97–1.82 (m, 2H), 1.78–1.65 (m, 3H), 1.57–1.47 (m, 3H), 1.31 (s, 3H), 0.83 (d, 3H, J = 6.9 Hz), 0.76 (d, 3H, J = 6.8 Hz); ^{13}C NMR (acetone-d_6) δ 155.4 (C), 155.0 (C), 143.3 (C), 136.9 (C), 128.4 (CH), 125.8 (CH), 115.2 (CH), 115.1 (CH), 48.5 (CH_2), 47.7 (CH), 42.7 (CH), 37.6 (CH_2), 36.9 (C), 27.2 (CH), 24.4 (CH_3), 20.9 (CH_3), 20.4 (CH_2), 14.9 (CH_3); FD MS m/z 324 (M^+).

(1α,3β,4α)-4,4′-[1-Methyl-4-(1-methylethyl)-1,3-cyclohexanediyl]bisphenol (3): ^{1}H NMR ($CDCl_3$) δ 7.24 (d, 2H, J = 8.7 Hz), 7.01 (d, 2H, J = 8.2 Hz), 6.79 (d, 2H, J = 8.3 Hz), 6.77 (d, 2H, J = 8.5 Hz), 4.89 (s, 1H), 4.85 (s, 1H), 2.45–2.29 (m, 3H), 1.61–1.15 (m, 6H), 1.10 (s, 3H), 0.74 (d, 3H, J = 7.0 Hz), 0.44 (d, 3H, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ 153.5 (C), 152.9 (C), 139.5 (C), 138.6 (C), 128.4 (CH), 127.5 (CH), 115.3 (CH), 115.2 (CH), 48.3 (CH), 47.9 (CH_2), 42.9 (CH), 38.9 (C), 37.8 (CH_2), 35.5 (CH), 27.3 (CH_3), 21.4 (CH_3), 21.0 (CH_2), 15.4 (CH_3).

(1α,3α,4β)-2-[1-[3-(4-Hydroxyphenyl)-4-methylcyclohexyl]-1-methylethyl]phenol (4): ^{1}H NMR ($CDCl_3$) δ 7.17 (d of d, 1H, J = 1.0, 8.0 Hz), 7.04 (d of d, 1H, J = 1.2, 7.0 Hz), 6.99 (d, 2H, J = 8.4 Hz), 6.83 (t, 1H, J = 7.1 Hz), 6.72 (d, 2H, J = 8.4 Hz), 6.62 (d, 1H, J = 7.2 Hz), 4.73 (s, 1H), 4.59 (s, 1H), 2.37 (t of t, 1H), 2.02 (t of d, 1H, J = 3.0, 10.2 Hz), 1.79 (m, 1H), 1.61 (m, 1H), 1.50–1.00 (m, 5H), 1.34 (s, 3H), 1.33 (s, 3H), 0.62 (d, 3H, J = 6.4 Hz); ^{13}C NMR ($CDCl_3$) δ 153.9 (C), 153.4 (C), 139.4 (C), 135.7 (C), 128.6 (CH), 128.4 (CH), 126.8 (CH), 120.5 (CH), 116.7 (CH), 115.0 (CH), 51.9 (CH), 44.0 (CH),

40.8 (CH), 38.1 (CH_2), 37.2 (CH_2), 36.2 (CH_2), 28.2 (CH_2), 24.7 (CH_3), 24.2 (CH_3), 20.4 (CH_3).

(1α,3α,4β)-2,4′-[1-Methyl-4-(1-methylethyl)-1,3-cyclohexanediyl]bisphenol (5): mp 144.0–146.0 °C (from chloroform); ^{1}H NMR ($CDCl_3$) δ 7.27 (d of d, 1H, J = 1.0, 8.0 Hz), 7.06 (d, 2H, J = 8.5 Hz), 7.05 (t, 1H, J = 8.0 Hz), 6.87 (t, 1H, J = 7.4 Hz), 6.75 (d, 2H, J = 8.3 Hz), 6.62 (d of d, 1H, J = 1.0, 8.1 Hz), 4.74 (s, 1H), 4.50 (broad s, 1H), 2.73 (t of d, 1H, J = 1.4, 6.0 Hz), 2.28–2.21 (m, 2H), 1.84–1.68 (m, 3H), 1.54–1.42 (m, 2H), 1.47 (s, 3H), 1.39–1.19 (m, 1H), 0.82 (d, 3H, J = 6,8 Hz), 0.75 (d, 3H, J = 6.7 Hz); ^{13}C NMR ($CDCl_3$) δ 154.1 (C), 153.5 (C), 138.8 (C), 137.5 (C), 128.7 (CH), 126.8 (CH), 126.5 (CH), 120.7 (CH), 116.8 (CH), 115.2 (CH), 47.9 (CH), 45.7 (CH_2), 42.5 (CH), 37.8 (C), 35.9 (CH_2), 27.4 (CH), 21.5 (CH_3), 21.3 (CH_3), 20.3 (CH_2), 15.5 (CH_3); FD MS m/z 324 (M^+).

(5α,6β,9α)-5,6,7,8,9,10-Hexahydro-2-hydroxy-6,10,10-trimethyl-5,9-methano-benzocyclooctene (6): ^{1}H NMR ($CDCl_3$) δ 6.85 (d, 1H, J = 8.5 Hz), 6.77 (d, 1H, J = 2.6 Hz), 6.58 (d of d, 1H, J = 2.6, 8.4 Hz), 5.17 (s, 1H), 2.53 (q, 1H, J = 1.5 Hz), 1.94 (d of t, 1H, J = 3.0, 13.0 Hz), 1.85 (d of q, 1H, J = 1.5, 13.0 Hz), 1.75–1.68 (m, 2H), 1.63 (d of t, 1H, J = 4.0, 13.4 Hz), 1.60–1.55 (m, 1H), 1.40–1.30 (m, 1H), 1.30 (s, 3H), 1.21 (s, 3H), 1.16 (d, 3H, J = 7.2 Hz), 0.98–0.92 (d of t, 1H, J = 1.4, 13.1 Hz); ^{13}C NMR ($CDCl_3$) δ 153.4 (C), 148.4 (C), 134.8 (C), 129.1 (CH), 112.8 (CH), 112.6 (CH), 41.0 (CH), 39.6 (CH), 36.8 (C), 35.9 (CH or CH_3), 35.2 (CH or CH_3), 27.4 (CH_3), 23.6 (CH_2), 23.5 (CH_2), 23.1 (CH_2), 18.2 (CH_3); IR (neat) 3318, 1616, 1455 cm^{-1}; FD MS m/z 230 (M^+).

(5α,6α,9α)-5,6,7,8,9,10-Hexahydro-2-hydroxy-6,10,10-trimethyl-5,9-methanobenzocyclooctene (7): ^{1}H NMR ($CDCl_3$) δ 6.79 (d, 1H, J = 2.5 Hz), 6.77 (d, 1H, J = 8.2 Hz), 6.54 (d of d, 1H, J = 2.6, 8.2 Hz), 4.72 (s, 1H), 2.62 (q, 1H, J = 1.9 Hz), 2.20 (d of q, 1H, J = 3.2, 12.5 Hz), 1.98 (d of m, 1H, J = 13.9 Hz), 1.75 (m, 2H), 1.61 (t, 1H, J = 3.1 Hz), 1.47 (t of t, 1H, J = 4.2, 13.8 Hz), 1.32 (s, 3H), 1.22 (s, 3H), 1.17 (m, 1H), 0.73 (d, 3H, J = 6.9 Hz), 0.67 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 153.7 (C), 149.4 (C), 131.1 (CH), 128.7 (C), 112.6 (CH), 111.5 (CH), 40.8 (CH), 39.0 (CH), 37.4 (CH), 37.2 (C), 35.6 (CH_3), 31.7 (CH_2), 29.6 (CH_2), 27.3 (CH_3), 26.6 (CH_2), 20.5 (CH_3); IR (neat) 3332, 1609, 1479 cm^{-1}.

(2α,5β,6α)-3,4,5,6-Tetrahydro-2-methyl-5-(1-methylethyl)-2,6-methano-2H-1-benzoxocin (8): ^{1}H NMR ($CDCl_3$) δ 7.08 (d of d of d, 1H, J = 1.6, 8.2, 8.3 Hz), 6.96 (d of d, 1H, J = 1.6, 7.6 Hz), 6.78 (d of d, 2H, J = 8.4, 8.6 Hz), 3.03 (q, 1H, J = 2.7 Hz), 1.87 (d of d, 1H, J = 2.5, 13.3 Hz), 1.82–1.70 (m, 2H), 1.65–1.55 (m, 2H), 1.48–1.40 (m, 2H), 1.34 (s, 3H), 1.20 (m, 1H), 1.06 (d, 3H, J = 6.6 Hz), 0.94 (d, 3H, J = 6.5 Hz); ^{13}C NMR ($CDCl_3$) δ 156.7 (C), 128.1 (CH), 127.7 (C), 127.2 (CH), 119.0 (CH), 115.0 (CH), 74.6(C), 47.4 (CH), 35.2 (CH_2), 34.6 (CH), 30.6 (CH_2), 29.4 (CH), 26.3 (CH_3), 22.0 (CH_3), 21.3 (CH_3), 19.9 (CH_2); IR (neat) 1607, 1582, 1152, 752 cm^{-1}; FD MS m/z 230 (M^+).

(2α,5β,6α)-3,4,5,6-Tetrahydro-5-methyl-2-(1-methylethyl)-2,6-methano-2H-1-benzoxocin (9): ^{1}H NMR ($CDCl_3$) δ 7.08 (d of d of d, 1H, J = 1.8, 8.0, 8.2 Hz), 6.98 (d of d, 1H, J = 1.3, 7.6 Hz), 6.78 (d, 1H, J = 8.4 Hz), 6.76 (d of d of d, 1H, J = 1.1. 8.2, 8.2 Hz), 2.71 (q, 1H, J = 2.6 Hz), 1.93 (d of d, 1H, J = 2.8, 13.0 Hz), 1.90 (m, 1H), 1.80 (p, 1H, J = 7.0 Hz), 1.71 (d of d, 1H, J = 4.4, 13.5 Hz), 1.67–1.53 (m, 3H), 1.20 (m, 1H), 1.13 (d, 3H, J = 7.2 Hz), 0.99 (d, 3H, J = 5.4 Hz), 0.97 (d, 3H, J = 5.2 Hz); ^{13}C NMR ($CDCl_3$) δ 156.7 (C), 128.4 (C), 128.0 (CH), 127.3 (CH), 118.8 (CH), 115.1 (CH), 79.2 (C), 38.7 (CH), 37.7 (CH), 34.8 (CH), 29.4 (CH_2), 24.5 (CH_2), 23.8 (CH_2), 17.8 (CH_3), 17.1 (CH_3), 17.0 (CH_3); IR (neat) 1605, 1589, 1125, 751 cm^{-1}; FD MS m/z 230 (M^+).

Diacetate of Bisphenol 1. A solution of bisphenol **1** (2.00 g, 6.17 mmol), acetic anhydride (40 mL), and concd sulfuric acid (0.25 mL) was stirred at ambient temperature for 3 h. The resulting solution was diluted with Et_2O and washed with water followed by a saturated NaCl solution. The dried ($MgSO_4$) organic phase was concentrated under vacuum (80 °C, 20 Torr) to give a yellow oil. Trituration with hexane gave a white crystalline solid, which was collected by filtration (2.4 g, 95% of theory). The diacetate of **1** was recrystallized from hexane: mp 112.0–113.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.29 (d, 2H, J = 8.7 Hz), 7.10 (d, 2H, J = 8.5 Hz), 6.99 (d, 2H, J = 8.6 Hz), 6.97 (s, 2H, J = 8.6 Hz), 2.26 (s, 6H), 2.04 (t of d, 1H, J = 1.9, 10.7 Hz), 1.82–1.55 (m, 3H), 1.46 (m, 1H), 1.25 (s, 6H), 1.20–0.99 (m, 3H), 0.62 (d, 3H, J = 6.4 Hz); ^{13}C NMR ($CDCl_3$) δ 169.6 (C), 169.5 (C), 148.7 (C), 148.3 (C), 147.3 (C), 144.1 (C), 128.3 (CH), 127.1 (CH), 121.2 (CH), 120.7 (CH), 52.0 (CH), 49.2 (CH), 40.1 (C), 37.7 (CH), 36.7 (CH_2), 35.8 (CH_2), 27.7 (CH_2), 25.9 (CH_3), 25.0 (CH_3), 21.2 (CH_3), 20.3 (CH_3); IR (neat) 3033, 1766, 1206 cm^{-1}.

Diacetate of Bisphenol 2. Following the same procedure used for **1**, the diacetate of bisphenol **2** was prepared in 87% yield: mp 132.0–133.0 °C; ^{1}H NMR ($CDCl_3$) δ 7.35 (d, 2H, J = 8.7 Hz), 7.18 (d, 2H, J = 8.4 Hz), 7.00 (d, 2H, J = 8.4 Hz), 6.98 (d, 2H, J = 8.7 Hz), 2.78 (m, 1H), 2.27 (s, 3H), 2.26 (s, 3H), 1.99 (m, 2H), 1.72 (m, 3H), 1.49 (m, 3H), 1.33 (s, 3H), 1.29 (m, 1H), 0.83 (d, 3H, J = 6.9 Hz), 0.75 (d, 3H, J = 6.7 Hz); ^{13}C NMR ($CDCl_3$) δ 169.6 (C), 169.5 (C), 149.6 (C), 148.8 (C), 148.4 (C), 143.5 (C), 128.4 (CH), 126.1 (CH), 121.3 (CH), 121.0 (CH), 47.9 (C), 47.6 (CH), 43.1 (CH), 37.5 (CH_2), 37.3 (CH_2), 27.3 (CH), 25.1 (CH_3), 24.9 (CH_3), 21.5 (CH_3), 21.2 (CH_3), 20.4 (CH_2), 15.4 (CH_3); IR (neat) 3050, 1765, 1205 cm^{-1}.

Methanolysis of Bisphenol 1 Diacetate. A mixture of the diacetate of bisphenol **1** (130 mg, 0.319 mmol), potassium carbonate (220 mg, 1.43 mmol) and methanol (30 mL) was stirred at rt for 2.5 h. The mixture was diluted with EtOAc, washed twice with water and once with a saturated NaCl solution, dried ($MgSO_4$) and concentrated to give 95 mg (92% of theory) of a white solid which was spectroscopically identical with bisphenol **1**.

Methanolysis of Bisphenol 2 Diacetate. The same procedure as described in the preceding experiment was followed to give bisphenol **2** in 93% yield.

Acid-Catalyzed Reaction of Bisphenol 1 and Phenol. A mixture of bisphenol **1** (1.00 g, 3.08 mmol), phenol (20.0 g, 213 mmol), and Amberlite 118 ion-exchange resin (2.00 g) was stirred at 100 °C. The progress of the reaction was monitored by HPLC, and after 4 d, the composition of the reaction contained equal amounts of **1** and one other product. The mixture was filtered to removed the ion-exchange resin, and the excess phenol was removed by distillation at reduced pressure. The residue was fractionated by flash column chromatography (25% EtOAc/hexane) to give recovered bisphenol **1** (0.38 g) and monophenol **6** (0.23 g).

Acid-Catalyzed Reaction of Bisphenol 2 and Phenol. Bisphenol **2** (1.00 g, 3.08 mmol) was reacted with phenol using the same procedure described in the previous reaction. The composition of bisphenols **2** and **3** was monitored by HPLC, and the percent of **2** present vs time is displayed in Figure 5. Product **3** was identified by HPLC coinjection with an authentic sample and characteristic signals in the ^{1}H NMR spectrum of the reaction mixture.

Acid-Catalyzed Reaction of Bisphenol 3. Bisphenol **3** (0.20 g, 0.616 mmol) was reacted with phenol, and the progress of the reaction was monitored using the procedure of the previous reaction.

Acid-Catalyzed Reaction of Bisphenol 4. Bisphenol **4** (0.10 g, 0.308 mmol) was reacted with phenol, and the progress of the reaction was monitored as described for the previous reaction.

Acid-Catalyzed Reaction of Bisphenol 5. Bisphenol **5** (0.20 g, 0.616 mmol) was reacted with phenol using the same procedure described for bisphenol **1**.

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Supplementary Material Available: ^{1}H- and ^{13}C-NMR spectra of **1**–**9** and the diacetates of **1** and **2** (22 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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