The mechanism of the Schiff base ozonation remains as the most perplexing of all of the carbon–nitrogen double-bond systems. The original product analysis data could be rationalized reasonably well by any of six different types of initial attack as noted above.[4a,5] The major problem with both product analysis and competitive ozonation studies lies in the reactivity of Schiff bases. They react very slowly with ozone but may react quite rapidly with ozonation products. Thus, although amides and oxaziridines are very likely primary products, they account for only 39% of products even in favorable cases, and major cleavage products may well be derived from secondary processes. Relative rate studies are also inconclusive. Originally we attempted to carry out competitive rate studies on benzaldehyde Schiff bases at −78° in methylene chloride. Ozonation was extremely slow; less than half of either Schiff base reacted in a 12-hr period. Dimethylhydrazones and oximes, on the other hand, react quantitatively with ozone at −78°. Thus, although the results in Table III are "real" in that they show Schiff bases to react considerably more slowly with ozone than do dimethylhydrazones, we believe the true relative rate spread may be considerably larger.[22] In other words, the decreasing concentration of Schiff base measured in our experiments may be caused by reaction with products of either the competing system or of the Schiff base itself.[23]

It has been believed generally that carbon–nitrogen double bonds are considerably less reactive than carbon–carbon double bonds. The data from these experiments appear to suggest, however, that carbon–nitrogen double-bond reactivity is dependent on the group attached to nitrogen. In fact *trans*-stilbene and acetophenone dimethylhydrazone have essentially equivalent rates of ozonation (competitive rate 1.01 ± 0.05).

Registry No.—Methyl nitrite, 624-91-9; acetophenone oxime, 613-91-2.

Acknowledgment.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(22) True rate comparisons could be made if experiments with stop-flow systems such as used by Williamson and Cvetanovic [D. G. Williamson and R. J. Cvetanovic, *ibid.*, **90**, 3668 (1968)] for alkene ozonations were carried out with dimethylhydrazones and oximes. The Schiff base ozonations are slow enough to be treated by conventional kinetic methods.

(23) A referee has suggested that nucleophilic attack on carbon to yield cleavage products may be competing with electrophilic bond attack on Schiff bases. The notion that ozone can act as a nucleophilic reagent is, of course, tantamount to calling it a reducing agent. Although such a situation is conceivable, we believe that rigorous proof would be necessary before postulating such a mechanism. As the proceeding paragraphs have indicated, such experimental justification is lacking.

New Carbonyl Compounds from Dehydrogenation of *p*-Cresol

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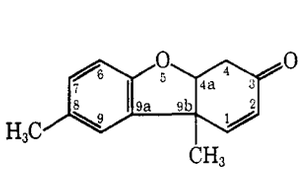
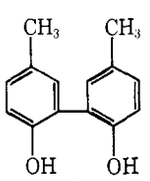
Chemical one-electron-type oxidation of *p*-cresol with ferric chloride yielded a previously unreported diphenyl ether **4** and three new ketonic trimers **5**, **6**, and **7**, the structures of which are related to Pummerer's ketone **1**, which was also formed in the reaction mixture as were the known compounds **2** and **3**. When *p*-cresol was oxidized enzymatically by peroxidase and peroxide, **5** was the only new unknown compound which could be isolated.

It is well established that the oxidation of *p*-cresol by one-electron-type chemical oxidants yields 4a,9b-dihydro-8,9b-dimethyl-3(4H)-dibenzofuranone (Pummerer's ketone) (**1**), 2,2′-dihydroxy-5,5′-dimethyldiphenyl (**2**), and 2,2′,2″-trihydroxy-5,5′,5″-trimethylterphenyl (**3**).[2-5] These products have also been isolated from the peroxidase-catalyzed oxidation of *p*-cresol with hydrogen peroxide.[6] A general review of the oxidative coupling of phenols, including *p*-cresol, and the significance of this type of reaction in biosynthesis have been published.[7]

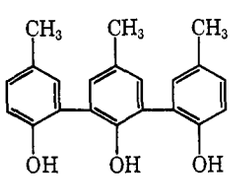
Hayes reported that in the oxidation of phenols by one-electron-type oxidants, more than 1 equiv of the oxidizing agent is consumed and that this must be the result of further oxidation of the low molecular weight products initially formed.[5] Mixtures of higher molecular weight substances were isolated in that work, but the constituents of the mixture were not identified. We have now oxidized *p*-cresol with 1.4 equiv of ferric chloride in aqueous solution, and have found that at least 10 compounds are present.



1



2



3

The reaction mixture was separated into alkali- and ether-soluble fractions, and further separation was

(1) (a) 1967 Summer Student Trainee, Forest Products Laboratory. (b) Maintained at Madison, Wis., in cooperation with the University of Wisconsin.

(2) R. Pummerer and F. Frankfurter, *Ber.*, **47**, 1472 (1913).

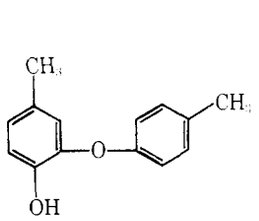
(3) R. Pummerer, H. Puttfarcken, and P. Schopflocher, *ibid.*, **58B**, 1808 (1925).

(4) D. H. R. Barton, A. M. Deflorin, and O. E. Edwards, *Chem. Ind.* (London), 1039 (1955).

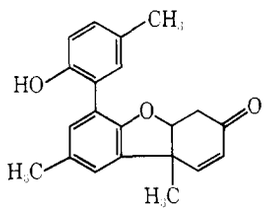
(5) C. G. Haynes, A. H. Turner, and W. A. Waters, *J. Chem. Soc.*, 2823 (1956).

(6) W. W. Westerfield and C. Lowe, *J. Biol. Chem.*, **145**, 463 (1942).

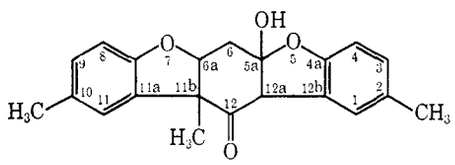
(7) A. I. Scott, *Quart. Rev.* (London), XIX, 1 (1965).



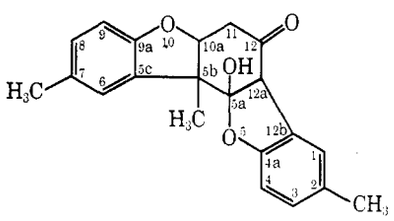
4



5



6

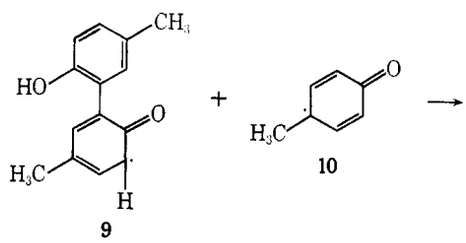


7

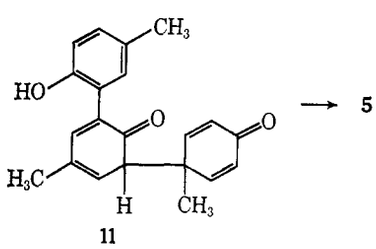
carried out by column chromatography on silicic acid and preparative tlc.

The alkali-soluble fraction contained **3** as the major product, a lesser amount of **2**, and a trace of 2-hydroxy-4′,5-dimethyl diphenyl ether (**4**), an *o-diphenyl* ether not previously isolated. The ether-soluble fraction contained **1**, **4**, and trimeric ketones, 6-(2′-hydroxy-5′-methylphenyl)-4a,9b-dihydro-8,9b-dimethyl-3(4H)-dibenzofuranone (**5**), 5a-hydroxy-5a,6a,11b,12a-tetrahydro-2,10,11b-trimethyl-12(6H)-benzo[1,2-*b*:5,4-*b*′]bisbenzofuranone (**6**), and 5a-hydroxy-5a,5b,10a,12a-tetrahydro-2,5b,7-trimethyl-12-(11H)-benzo[1,2-*b*:3,4-*b*′]bisbenzofuranone (**7**). A tetrameric ketone, **8**, $C_{28}H_{26}O_5$, was also isolated from the ether fraction, but the exact structure of this compound could not be determined. It is interesting that in the enzymatic dehydrogenation of *p*-cresol with peroxidase and peroxide catalyst, compounds **1**, **2**, **3**, **4**, and **5** were shown to be present, but **6**, **7**, and **8** could not be detected.

The formation of **5** could take place through the coupling of an *ortho* radical, **9**, from the dehydrogenation of **2** with a *para* radical from *p*-cresol (**10**) to give the intermediate **11**, which could then cyclize to **5**.

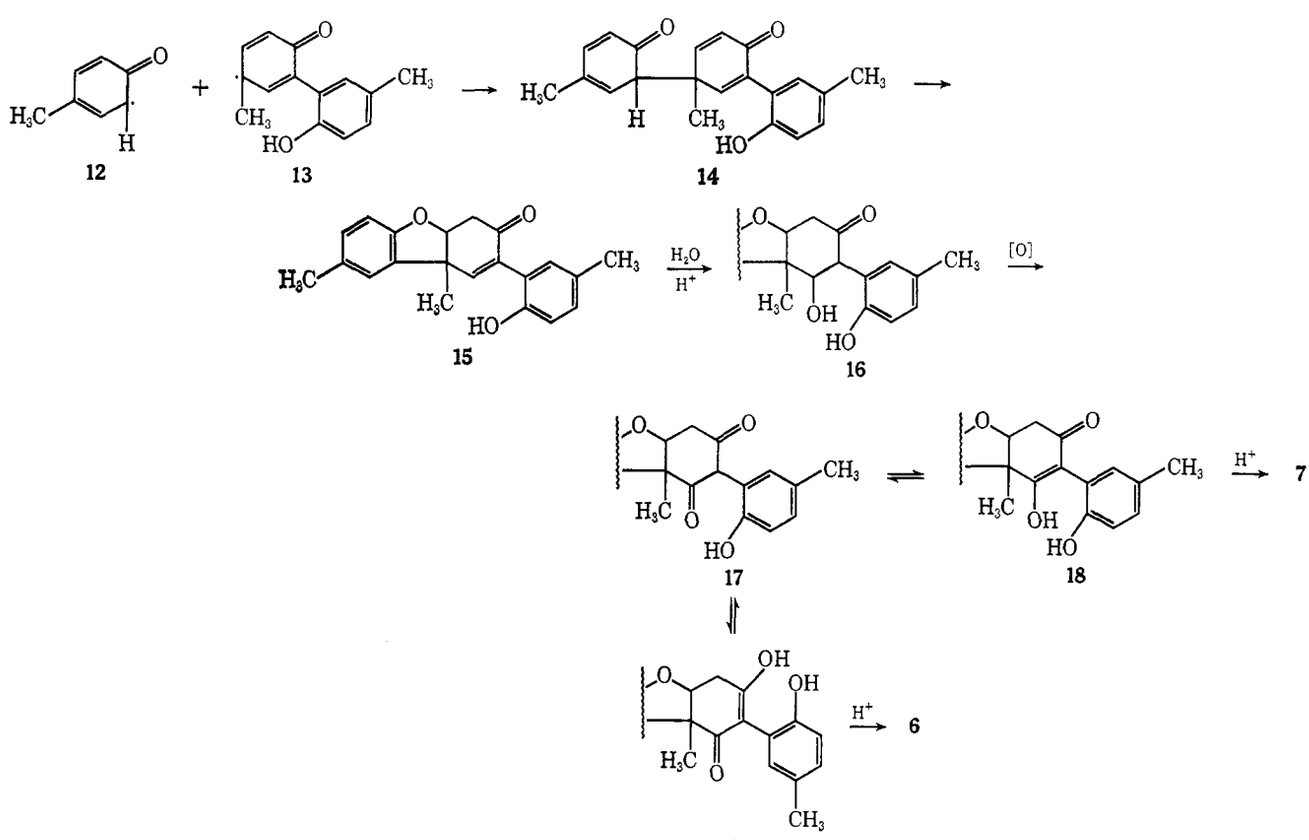


9 10



11

The formation of **6** and **7** in the ferric chloride oxidation could take place through the coupling of an *ortho* radical, **12**, formed from the oxidation of *p*-cresol with a *para* radical, **13**, formed from the oxidation of **2** to give



12 13 14

15 16

17 18 7

19 6

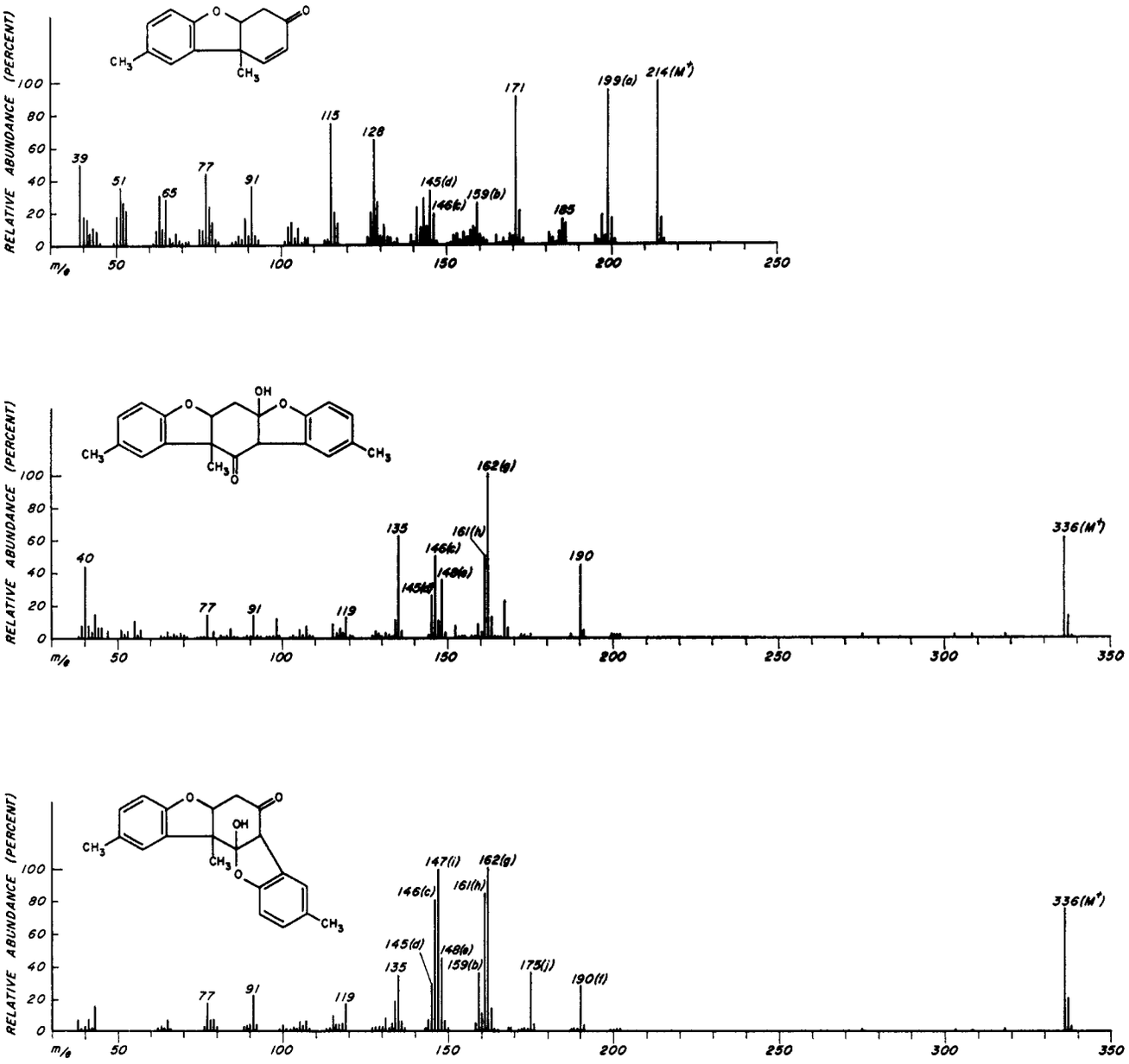


Figure 1.—Mass spectra of compounds **1**, **6**, and **7**.

the intermediate trimer **14**, which could then cyclize to **15**. From **15** to **6** and **7**, the sequences would then be the addition of water and oxidation of the resulting β-hydroxyketo compound **16** to the β-diketo compound **17** which has enol tautomers **18** and **19**. These, under the influence of acid, could cyclize to form hemiacetals **6** and **7**.

The mass spectrum of **1** (Figure 1, Scheme I) showed prominent peaks corresponding to the molecular ion M $-$ CH_3 and M $-$ (CH_3 + CO) ions. Loss of a methyl radical from the molecular ion caused by α fission of the substituted coumaran at C-9b afforded the stable ion at *m/e* 199 (a) which gave the ion at *m/e* 171 through further loss of carbon monoxide. Breakdown of the molecular ion at ring junctures C-4a and C-9b gave the ion at *m/e* 146 (c) which loses a hydrogen atom to produce the stable ion at *m/e* 145 (d).[8] Alternative breakdown of the molecular ion at C-4 and C-9b with hydrogen transfer and elimination of C_3H_3O could produce the ion at *m/e* 159 (b). This required α fission of the substituted coumaran at C-9b and a subsequent McLafferty rearrangement involving the C-4a hydrogen. The vinylic cleavage was presumably induced by the allylic stabilization of the coumaran ring; this may not be intrinsically unfavorable. 4-Alkyl- or aryl-Δ^2-cyclohexanone derivatives exhibit a characteristic M $-$ 42 ion peak on electron impact.[9] Absence of this ion peak in the mass spectrum of Pummerer's ketone, and the presence of the ions b and c, should be regarded as caused by the effect of the coumaran moiety fused to the cyclohexanone.

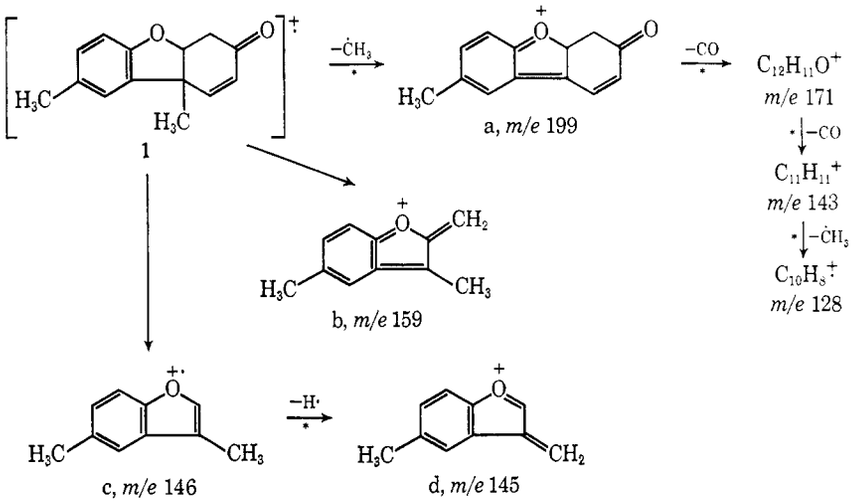
The nuclear magnetic resonance spectrum of **5** was similar to **1**,[10] and consistent with the structure presented for this compound. The C-4 geminal protons and the C-4a proton constitute an ABX spin pattern with coupling constants J_{AB} = 18.0 Hz, J_{AX} = 3.0 Hz, and J_{BX} = 4.0 Hz. The X component is further

(8) B. Willhalm, A. F. Thomas, and F. Gautschi, *Tetrahedron*, **20**, 1185 (1964).

(9) A. L. Burlingame, C. Fenselau, W. J. Richter, W. G. Dauben, G. W. Shaffer, and N. D. Vietmeyer, *J. Amer. Chem. Soc.*, **89**, 3346 (1967).

(10) J. Shoji, *Chem. Pharm. Bull.* (Tokyo), **10**, 483 (1962).

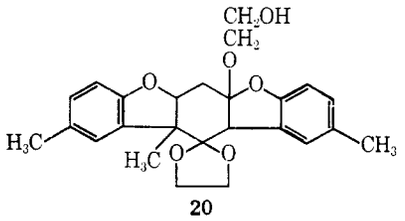
SCHEME I[a]



[a] Transitions substantiated by an appropriate metastable peak are indicated by an asterisk.

split by the C-1 olefinic proton (J = 1.8 Hz) because of long-range four-bond σ–π spin–spin interactions which had been reported earlier for **1**.[11] The mass spectrum of **5** showed a strong molecular ion peak and less abundant ion peaks corresponding to M − CH_3 and M − (CH_3 + CO), as in **1**.

Trimeric ketone **6** had a molecular formula $C_{21}H_{20}O_4$ which contained one oxygen atom more than the expected trimeric dehydrogenative condensation product of *p*-cresol. The infrared spectrum of the compound showed the presence of a hydroxyl group (3470 cm^{-1}) and a six-membered cyclic ketone (1721 cm^{-1}). In the nmr spectrum in deuteriochloroform, the alicyclic protons were not well resolved. However, in pyridine, **6** did give a first-order spectrum compatible with the structure presented. A two-proton doublet (J = 3.2 Hz) at δ 3.25 (C-6) and a one-proton triplet (J = 3.2 Hz) at δ 4.78 (C-6a) constituted a characteristic A_2X system.[10] The one-proton singlet at δ 4.98 (C-12a) was caused by the β-proton of a coumaran adjacent to a carbonyl group.[12] In deuteriochloroform the signals for C-6a and C-12a protons merged at δ 4.65, whereas signals for C-6 geminal protons appeared as a multiplet at δ 3.25, although no distinct geminal coupling could be observed. This could be attributed to absence of π-bond contribution and to the electronegative groups substituted on the carbon atom adjacent to the C-6 methylene group.[13] When **6** was refluxed with ethylene glycol under the catalytic influence of *p*-toluenesulfonic acid, it reacted with 2 mol of ethylene glycol to afford β-hydroxyethyl ether ethylene ketal **20**. This furnished a proof of the hemiacetal structure of **6**.



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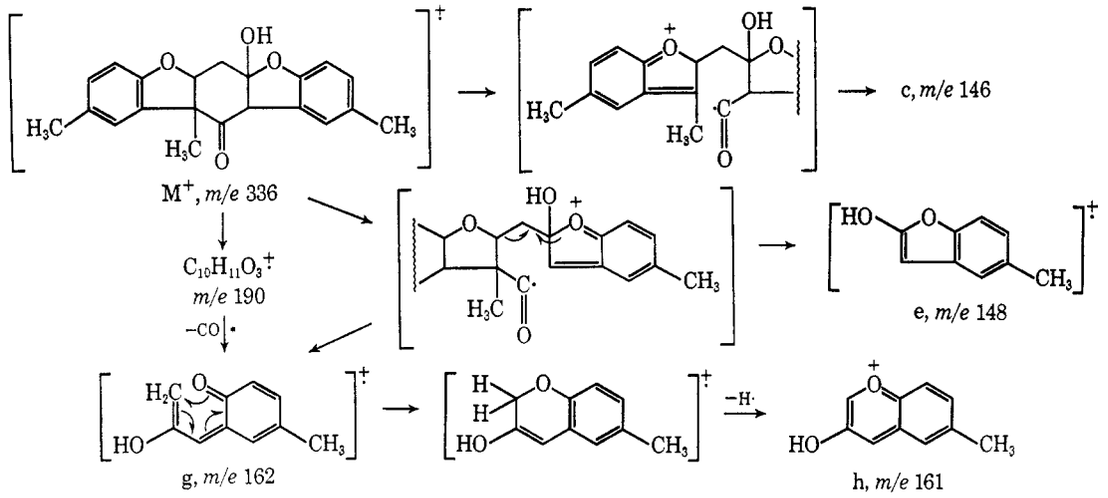
A further support of the structure of **6** was obtained by the mass spectrum (Figure 1, Scheme II). Breakdown of the molecular ion at ring juncture either at C-11b or C-12a caused by α fission of coumaran and subsequent allylic cleavage produced the ions at *m/e* 146 (c) and 148 (e), which retained the skeletons of both coumaran moieties. Alternative breakdown of the molecular ion at C-12a and C-6a with ether cleavage afforded the ion at *m/e* 162 (g) which cyclized and aromatized by loss of a hydrogen atom to give the ion at *m/e* 161 (h). The latter reaction bears close analogy to the cyclization reaction in 2-(β-butenyl)benzoquinone derivatives[14] and the cyclization of benzalacetone derivatives.[15] Expulsion of a neutral fragment corresponding to c from the molecular ion gave the ion at *m/e* 190. Loss of carbon monoxide from this ion at *m/e* 190 also produced the ion g, indicated by the metastable peak at *m/e* 138.2.

Trimeric ketone **7** also had molecular formula $C_{21}H_{20}O_4$, and gave a uv spectrum which resembled that of **6**. This, with an infrared spectrum which showed a hydroxyl band at 3440 cm^{-1} and a six-membered cyclic ketone band at 1735 cm^{-1}, revealed that the compound was an isomer of **6**. The higher carbonyl frequency was indicative of ring strain caused by fusion of additional rings to cyclohexanone.[16] In the nmr spectrum, the alicyclic protons showed a different splitting pattern from that of **6**. Two one-proton quartets (C-11 geminal protons) with resonance centers at δ 2.50 (J = 19.4 and 3.8 Hz) and at δ 2.95 (J = 19.4 and 2.6 Hz) and a one-proton multiplet (J = 3.8 and 2.6 Hz) at δ 4.46 (C-10a) constituted a characteristic ABX system. A one-proton singlet at δ 4.72 was caused by a C-12a proton. The large geminal coupling constant indicated a large π-bond contribution from the carbonyl group adjacent to the methylene group. This also indicated a ring strain of the cyclohexanone ring caused by two adjacent coumaran rings.

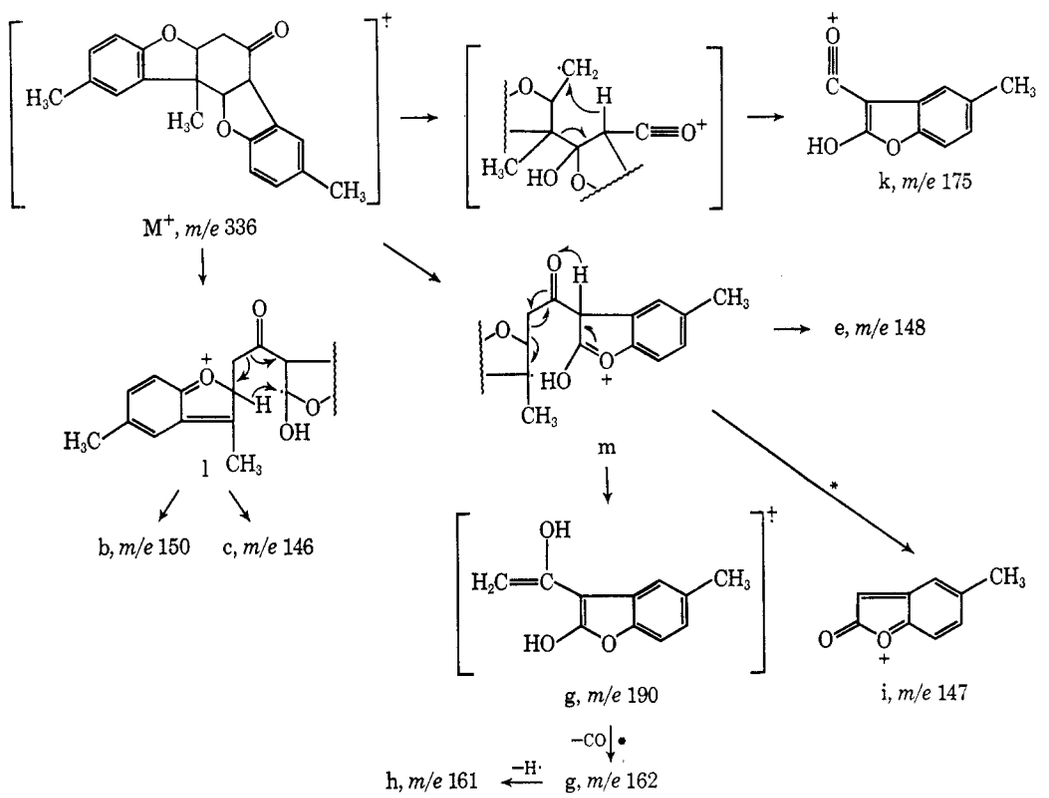
When the compound was refluxed with ethylene glycol under the catalytic influence of *p*-toluenesulfonic acid, it reacted with 1 mol of ethylene glycol with elim-

(11) G. W. Kirby and H. P. Tiwari, *J. Chem. Soc.*, 4655 (1964).
(12) A. Stoessl, *Can. J. Chem.*, **45**, 1745 (1967).
(13) M. Barfield and D. M. Grant, *J. Amer. Chem. Soc.*, **85**, 1899 (1963).
(14) S. J. Di Mari, J. H. Supple, and H. Rapoport, *ibid.*, **88**, 1226 (1966).
(15) J. Ronayne, D. H. Williams, and J. H. Borwie, *ibid.*, **88**, 4980 (1966).
(16) C. F. H. Allen, T. Davis, D. W. Stewart, and J. A. VanAllan, *J. Org. Chem.*, **20**, 306 (1955).

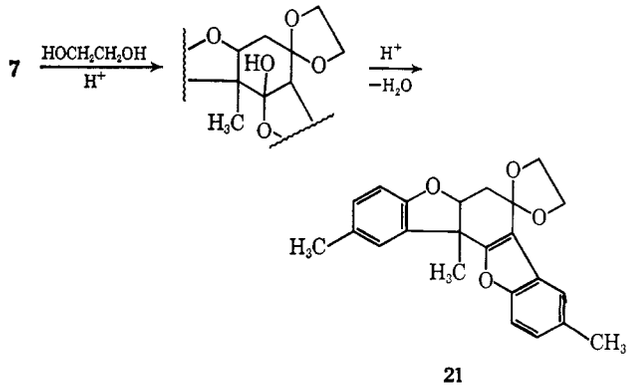
SCHEME II



SCHEME III



ination of 2 mol of water to afford the compound **21**. Elimination of water could result from the formation of the ethylene ketal followed by dehydration involving the hemiacetal hydroxy as such, or by loss of ethylene glycol from the β-hydroxyethyl ether of the ethylene ketal of **7**, which could form in this reaction medium.



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The mass spectrum of **7** (Figure 1, Scheme III) was considerably different from that of **6**. In addition to the important ion peaks which appeared in **6**, **7** contained a very strong peak at *m/e* 147 and two moderate ion peaks at *m/e* 175 and 159. A breakdown of the molecular ion at ring juncture C-5a caused by α fission of the coumaran ring could produce two intermediates, l and m. Elimination of a neutral fragment corresponding to c from m gave the ion at *m/e* 190, which might have structure f. Loss of carbon monoxide from the f ion produced the ion at *m/e* 162 (g).[17] An alternative allylic cleavage afforded the ion at *m/e* 148 (e). The ion at *m/e* 147 (i) could arise

(17) R. Grigg, H. J. Jakobsen, S.-O. Lawesson, M. V. Sargent, G. Schroll, and D. H. Williams, *J. Chem. Soc., B*, 331 (1966).

from the ion e by the loss of a hydrogen atom. However, the metastable peak at *m/e* 64.4 indicated that the ion at *m/e* 147 was produced from the molecular ion. Hydrogen transfer caused by allylic stabilization probably took place during the allylic cleavage. An allylic cleavage of the intermediate l produced the ion at *m/e* 146 (c), whereas a McLafferty rearrangement involving C-10a gave the ion at *m/e* 159 (b). The formation of the ion at *m/e* 175 (k) was caused by α cleavage of carbonyl and subsequent McLafferty rearrangement.

Experimental Section

Nmr spectra were determined on a Varian HA-100 instrument. Chemical shifts are reported in δ values relative to tetramethylsilane standard. The mass spectrum of 1 was determined on an AEI MS 12 mass spectrometer, others on an Atlas CH-4.

Dehydrogenation of p-Cresol with Ferric Chloride.—*p*-Cresol (10.5 g) and ferric chloride hexahydrate (32.5 g) were stirred together in water (1.5 l.) for 72 hr at room temperature; the solution changed color from orange to green. The reaction mixture was made alkaline and extracted with ether. The ether solution was then examined by tlc and showed 10 substances present, with 4a,9b-dihydro-8,9b-dimethyl-3(4H)-dibenzofuranone (1) the major product. A total of 1.16 g of alkaline-insoluble material was obtained.

Dehydrogenation of p-Cresol with Peroxidase Peroxide.—A mixture of 10.8 g (0.1 equiv) of *p*-cresol and 50 mg of horseradish peroxidase was dissolved in 100 ml of 50% aqueous ethanol. While the mixture was stirred for 30 min, 17 ml of 1% H_2O_2 (0.1 equiv) was added, and then the mixture was stirred for an additional 60 min. The mixture was allowed to stand overnight and separated into neutral and alkaline-soluble fractions as in the dehydrogenation of *p*-cresol with ferric chloride.

5a-Hydroxy-5a,6a,11b,12a-tetrahydro-2,10,11b-trimethyl-12(6H)-benzo[1,2-*b*:5,4-*b*']bisbenzofuranone (6).—The reaction mixture (5.8 g) from the ferric chloride dehydrogenation was dissolved in 30 ml of cold acetone. The insoluble residue was collected, washed with cold acetone (three 5-ml portions), and recrystallized from $CHCl_3$; white plates (121 mg) were obtained, mp 252–253°; uv λ_{max} (95% EtOH) 288 (ϵ 5.34 × 10^3) and 294 mμ (ϵ 5.11 × 10^3); λ_{max} (95% EtOH + 1 drop/ml of 1 *N* EtONa) 300 mμ (ϵ 7.11 × 10^3); ir (KBr) 3470 (OH), 3025 (ArH), 2960, 2920, 2860 (CH_3), 1720 (C=O), 1612, 1490 (ArH) cm^{-1}; nmr ($CDCl_3$) δ 1.44 (s, 3, Anu-CH_3), 2.21 (s, 3, ArCH_3), 2.28 (s, 3, ArCH_3), 3.25 (m, 2, OCHCH_2COO), 4.42 (s, 1, OH, eliminated by exchange with D_2O), 4.64 (m, 1, OC**H**CH_2), 4.65 (s, 1, OCC**H**Ar), 6.44 (d, 1, *J* = 8.0 Hz, Ar**H**), 6.54 (d, 1, *J* = 8.2 Hz, Ar**H**), 6.86 (m, 2, *J* = 2.2, 8.2 Hz, Ar**H**), 6.97 (s, 1, Ar**H**), 7.39 (d, 1, *J* = 2.2 Hz, Ar**H**); nmr (pyridine) δ 1.35 (s, 3, Anu-CH_3), 1.98 (s, 3, ArCH_3), 2.10 (s, 3, ArCH_3), 3.25 (d, 2, *J* = 3.2 Hz, OCHCH_2COO), 4.62 (s, 1, OH, eliminated by exchange with D_2O), 4.78 (t, 1, *J* = 3.2 Hz, OC**H**CH_2), 4.98 (s, 1, OCC**H**Ar), no aromatic protons could be analyzed owing to pyridine.

Anal. Calcd for $C_{21}H_{20}O_4$: C, 74.98; H, 5.99. Found: C, 74.93; H, 6.12.

5a-(β-Hydroxyethoxy)-5a,6a,11b,12a-tetrahydro-2,10,11b-trimethyl-12(6H)-benzo[1,2-*b*:5,4-*b*']bisbenzofuranone Ethylene Ketal (20).—A mixture of 5a-hydroxy-5a,6a,11b,12a-tetrahydro-2,10,11b-trimethyl-12(6H)-benzo[1,2-*b*:5,4-*b*']bisbenzofuranone (6) (40 mg), *p*-toluenesulfonic acid (20 mg), toluene (15 ml), and ethylene glycol (4 ml) was heated at reflux temperature with continuous slow removal of the solvent for 6 hr. After cooling, a few drops of pyridine were added to the reaction mixture to neutralize the acid. The organic phase was extracted with ether, washed with distilled water, dried, and evaporated *in vacuo*. The residue (recrystallized from methanol–acetone) was white rhombic crystals (18 mg), mp 208–210°; uv λ_{max} (95% EtOH) 282 and 289 mμ; ir (KBr) 3520 (OH), 2942 and 2892 (CH_3 and $-CH_2-$), 1620, 1500 (ArH); nmr ($CDCl_3$) δ 1.54 (s, 3, Anu-CH_3), 2.25 (s, 3, ArCH_3), and 2.30 (s, 3, ArCH_3).

Anal. Calcd for $C_{25}H_{28}O_6$: C, 70.78; H, 6.60; M^+ *m/e* 424.18859. Found: C, 70.59; H, 6.49; M^+ *m/e* 424 (low resolution).

4a,9b-Dihydro-8,9b-dimethyl-3(4H)-dibenzofuranone (Pummerer's Ketone) (1).—After 5a-hydroxy-5a,6a,11b,12a-tetrahydro-2,10,11b-trimethyl-12(6H)-benzo[1,2-*b*:5,4-*b*']bisbenzofuranone (6) was crystallized from the neutral fraction, Pummerer's ketone (1) was isolated by column chromatography on silicic acid with chloroform–cyclohexane (4:1) as solvent and purified by preparative tlc on silica gel: mp 124–125° (lit.[2] mp 124°).

Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.53; H, 6.58. Found: C, 78.48; H, 6.59.

2-Hydroxy-4',5-dimethyl Diphenyl Ether (4).—This compound was isolated as an oil in the same manner as Pummerer's ketone (1). It had uv λ_{max} (95% EtOH) 278 and 283.5 mμ; λ_{max} (95% EtOH + 1 drop/ml of 1 *N* EtONa) 287.5 and 302 mμ; ir (film) 3525, 3450 (OH), 3035 (ArH), 2920, 2860 (CH_3), 1600, 1510 (ArH), 1278 (ArO), 1225 cm^{-1} (phenolic CO); nmr ($CDCl_3$) δ 2.14 (s, 3, ArCH_3), 2.26 (s, 3, ArCH_3), 5.50 (s, 1, OH, eliminated by D_2O), 6.6–7.3 (seven aromatic protons); mass spectrum (70 eV) *m/e* (rel intensity) 215 (12.7), 214 (100), 198 (23), 197 (5), 183 (6), 123 (5), 107 (12.5), 94 (15), 92 (24), 91 (23), 78 (12), 77 (12), 66 (8), 65 (13), 52 (5), 51 (9), 41 (5), 39 (12).

6-(2'-Hydroxy-5'-methylphenyl)-4a,9b-dihydro-8,9b-dimethyl-3(4H)-dibenzofuranone (5).—The compound was isolated and purified in the same manner as Pummerer's ketone (1); it formed white needles (34 mg), mp 135–136°; uv λ_{max} (95% EtOH) 299 mμ (ϵ 6.49 × 10^3); λ_{max} (95% EtOH + 1 drop/ml of 1 *N* EtONa) 321 mμ (ϵ 7.86 × 10^3); ir (KBr) 3395 (OH), 3015 (ArH), 2970, 2925, 2860 (CH_3), 1675 (C=C—C=O), 1620, 1500 (ArH), 1260 (OH), 802 (*cis*-CH=CH—) cm^{-1}; nmr ($CDCl_3$) δ 1.60 (s, 3, Anu-CH_3), 2.30 (s, 3, ArCH_3), 2.37 (s, 3, ArCH_3), 2.76 (m, 1, *J* = 4.0, 18.0 Hz, $CHCH_AH_BCO$), 3.08 (m, 1, *J* = 3.0, 18.0 Hz, $CHCH_AH_BCO$), 4.82 (m, 1, *J* = 1.8, 3.0, 4.0 Hz, $ArOCHCH_AH_B$), 5.95 (d, 1, *J* = 10.4 Hz, CH=C**H**CO), 6.04 (s, 1, OH, eliminated by exchange with D_2O), 6.50 (m, 1, *J* = 1.8, 10.4 Hz, C**H**=CHCO), 6.90 (d, 1, *J* = 8.8 Hz, Ar**H**), 7.07 (m, 4, Ar**H**); mass spectrum *m/e* (rel intensity) 321 (25.5), 320 (100), 305 (17), 303 (5), 302 (5.5), 287 (8.5), 277 (10.5), 212 (5.5), 211 (6.5), 166 (5), 115 (5), 77 (5), 43 (6).

Anal. Calcd for $C_{21}H_{20}O_3$: C, 78.75; H, 6.25. Found: C, 78.70; H, 6.30.

5a-Hydroxy-5a,5b,10a,12a-tetrahydro-2,5b,7-trimethyl-12(11H)-benzo[1,2-*b*:3,4-*b*']bisbenzofuranone (7).—This compound was isolated and purified in the same manner as Pummerer's ketone (1). The compound was recrystallized from methanol, yielding white needles (106 mg), mp 208–209°; uv λ_{max} (95% EtOH) 287.4 (ϵ 5.98 × 10^3) and 293.4 mμ (ϵ 5.58 × 10^3); λ_{max} (95% EtOH + 1 drop/ml of 1 *N* EtONa) 242 (ϵ 1.42 × 10^4) and 304 mμ (ϵ 6.87 × 10^3); ir (KBr) 3440 (OH), 3025 (ArH), 2970, 2925, 2865 (CH_3), 1735 (C=O), 1615, 1494 (ArH) cm^{-1}; nmr ($CDCl_3$) δ 1.49 (s, 3, Anu-CH_3), 2.36 (s, 6, ArCH_3), 2.50 (m, 1, *J* = 3.8, 19.4 Hz, $OCHCH_AH_BCO$), 2.95 (m, 1, *J* = 2.6, 19.4 Hz, $OCHCH_AH_BCO$), 4.28 (s, 1, OH, eliminated by exchange with D_2O), 4.45 (m, 1, *J* = 2.6, 3.8 Hz, OC**H**CH_2), 4.72 (s, 1, OCC**H**Ar), 6.71 (d, 1, *J* = 7.8 Hz, Ar**H**), 6.82 (d, 1, *J* = 8.0 Hz, Ar**H**), 6.92 (m, 1, Ar**H**), 6.99 (m, 1, Ar**H**), 7.08 (m, 1, *J* = 2.2, 8.0 Hz, Ar**H**), 7.62 (d, 1, *J* = 2.2 Hz).

Anal. Calcd for $C_{21}H_{20}O_4$: C, 74.98; H, 5.99. Found: C, 75.19; H, 5.95.

5b,10a-Dihydro-2,5b,7-trimethyl-12(11H)-benzo[1,2-*b*:3,4-*b*']bisbenzofuranone Ethylene Ketal (21).—5a-Hydroxy-5a,5b,10a,12a-tetrahydro-2,5b,7-trimethyl-12(11H)-benzo[1,2-*b*:3,4-*b*']bisbenzofuranone (7) (40 mg) was treated according to the procedure for the preparation of 5a-(β-hydroxyethoxy)-5a,6a,11b,12a-tetrahydro-2,10,11b-trimethyl-12(6H)-benzo[1,2-*b*:5,4-*b*']bisbenzofuranone ethylene ketal (20). This yielded white needles (16 mg), mp 178–180°; uv λ_{max} (95% EtOH) 287 and 294 mμ; ir (KBr) 3010 (ArH), 2970, 2925, 2880 (CH_2 and CH_3), 1617, 1495 cm^{-1} (ArH); nmr ($CDCl_3$) δ 1.16 (s, 3, Anu-CH_3) and 2.28 (s, 6, ArCH_3).

Anal. Calcd for $C_{23}H_{22}O_4$: C, 76.24; H, 6.08; M^+ *m/e* 362.15181. Found: C, 76.19; H, 6.15; M^+ *m/e* 362 (low resolution).

Registry No.—*p*-Cresol, 106-44-5; **1**, 546-24-7; **4**, 10568-14-6; **5**, 21272-73-1; **6**, 21272-74-2; **7**, 21272-75-3; **20**, 21272-76-4; **21**, 21272-77-5.

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