

Figure 10. The optical spectrum of 9-mesitylfluorenyl free radical.

hydrogens of the fluorenyl system. The splitting is *ca.* 2 G. The major conclusion drawn from the complex spectrum obtained under high resolution is that there is no line at the center of the spectrum. This requires that there be one group which causes a splitting into an even number of lines and this group must have

an odd number of protons. All protons in the 9-mesitylfluorenyl radical occur in pairs or in even multiples with the sole exception of the *p*-methyl group. There must be some spin density in the mesityl ring but it is probably not large.

The radical is quite stable in solution and the esr spectrum did not change in intensity upon cooling below room temperature, which indicates that dimerization does not occur. It reacts with oxygen but much more slowly than triphenylmethyl reacts. When a degassed solution of the radical was aerated thoroughly for a few minutes the only noticeable change in the esr spectrum was line broadening attributable to dissolved oxygen. Longer exposure to air caused decomposition with the formation of a red solution whose composition was not studied.²⁵

Acknowledgments. We thank Dr. S. H. Glarum and J. H. Marshall for determining the esr spectra and for discussions of them. We are especially grateful to Dr. M. Cocivera for informative discussions of exchange in nmr spectroscopy.

(25) NOTE ADDED IN PROOF. Professor H. Volz of the University of Karlsruhe has informed us (May 1968) that he and Miss B. Schelberger have made related studies of various 9-arylfluorene-9 cations which will be published shortly in *Chemische Berichte*. Professor Volz also called our attention to a previous report of the 9-mesitylfluorenyl radical (W. Theilacker, *et al.*, *Angew. Chem.*, **69**, 322 (1957)) which, unfortunately, is not indexed in *Chemical Abstracts*.

Electron Paramagnetic Resonance and Electron-Nuclear Double Resonance Studies of Phenoxy Radicals Derived from Substituted Diphenylmethanes

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Abstract: A series of five oxidized diphenylmethane derivatives related to the free radical galvinoxyl has been prepared. The four *t*-butyl groups are replaced by several combinations of methyl, methoxyl, and *t*-butyl groups. Two of these compounds are new and their syntheses involved some interesting reactions and side products; a quinone methide intermediate is proposed to account for these. Electron-nuclear double resonance (ENDOR) and electron paramagnetic resonance (EPR) spectra of these compounds in solution have been obtained with the following results. (a) All proton hyperfine couplings have been determined and a previously published assignment for the compound with all *t*-butyls replaced by methoxyls has been corrected. (b) In order to interpret the spectra, molecular orbital calculations have been carried out treating the methyl, *t*-butyl, and methoxyl groups by the "heteroatom model." The parameters to describe the methyl and *t*-butyl groups are found to be nearly identical ($h_X = 2.0$, $k_{C-X} = 0.7$), but the methoxyl group is best treated by $h_X = 2.2$ and $k_{C-X} = 0.6$. (c) When the two *t*-butyl groups on one of the rings are replaced by methyl groups, the methyls are inequivalent. This molecular asymmetry results in a splitting of the methyl proton ENDOR line. If a perturbation is introduced into molecular orbital calculations for the various molecules which is sufficient to cause the observed splitting in this molecule, the resulting splittings of all of the other ENDOR lines of this series are calculated to be below detectability. (d) If one *t*-butyl of each ring is replaced by a methyl, two isomers yielding separate ENDOR spectra exist in solution, and an approximate activation energy of 1 kcal/mol has been obtained describing the interconversion of the isomers.

The free radical galvinoxyl (I) (sometimes referred to as Coppinger's radical) was prepared by Coppinger² and Kharasch³ in 1957. This radical possesses re-

markable stability, both in the solid state and when dissolved in various organic solvents. It has been the subject of several electron paramagnetic resonance

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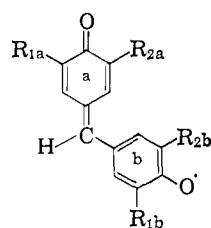
(2) G. M. Coppinger, *J. Amer. Chem. Soc.*, **79**, 501 (1957).

(3) M. S. Kharasch and B. S. Joshi, *J. Org. Chem.*, **22**, 1435 (1957).

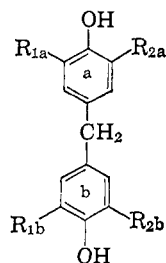
(epr) studies⁴⁻⁶ and has also been investigated by electron-nuclear double resonance (ENDOR) techniques.^{7,8}

Recently, the lignin degradation product syrioxyl (II) was reported⁹ to be a free radical with stability in the solid state approaching that of I. The replacement of all four *t*-butyl groups by methoxyl groups (I to II) conferred some unusual properties on this quinone methide radical. Its diphenylmethane precursor VII is somewhat water soluble and could conceivably give rise to II by weathering or fungal attack on woody tissues. (For example, II can be generated readily from VII in aqueous solutions by peroxidase and peroxide, in which system its half-life is 6 min.)¹⁰

We have now prepared some further diphenylmethane precursors which are related to VII, compounds VIII-XI, and have succeeded in making the corresponding free radicals III, IV, and V, but were unsuccessful in making VI. The synthesis of the precursors is given in the last section of this paper, together with a discussion of some of the related chemistry.



I-VI



VII-XI

I, $R_{1a} = R_{2a} = R_{1b} = R_{2b} = t\text{-butyl}$
 II, $R_{1a} = R_{2a} = R_{1b} = R_{2b} = \text{OCH}_3$
 III, $R_{1a} = R_{2a} = t\text{-butyl}$; $R_{1b} = R_{2b} = \text{OCH}_3$
 IV, $R_{1a} = R_{2a} = t\text{-butyl}$; $R_{1b} = R_{2b} = \text{CH}_3$
 V, $R_{1a} = R_{2b} = t\text{-butyl}$; $R_{2a} = R_{1b} = \text{CH}_3$
 VI, $R_{1a} = R_{2a} = R_{1b} = R_{2b} = \text{CH}_3$

VII, $R_{1a} = R_{2a} = R_{1b} = R_{2b} = \text{OCH}_3$
 VIII, $R_{1a} = R_{2a} = t\text{-butyl}$; $R_{1b} = R_{2b} = \text{OCH}_3$
 IX, $R_{1a} = R_{2a} = t\text{-butyl}$; $R_{1b} = R_{2b} = \text{CH}_3$
 X, $R_{1a} = R_{2b} = t\text{-butyl}$; $R_{2a} = R_{1b} = \text{CH}_3$
 XI, $R_{1a} = R_{2a} = R_{1b} = R_{2b} = \text{CH}_3$

In the next section of this paper we present ENDOR spectra of compounds II-V. The ENDOR technique, which is reviewed briefly in that section, may be viewed operationally as a physical method yielding the same spectral information as EPR, but with improved resolution. Even though these compounds are relatively simple, the ENDOR experiments have yielded several notable results which we think could not have been obtained from the EPR spectra, and have confirmed other results which perhaps could have been obtained, but with some uncertainty.

This paper has four somewhat intermixed themes. First, there was a problem in the interpretation of the EPR spectrum of II. All 12 methoxyl protons couple strongly with the free electron. The original interpretation⁹ of the 130-line EPR spectrum indicated that six of the methoxyl protons were not equivalent to the other six (see Table I). This interpretation was questioned

Table I. Hyperfine Coupling Constants (in gauss)

Proton	I ^a	II ^b	II ^c
Methide	5.57	5.60	5.6
Ring	1.38	0.14	1.4
Substituent	0.03	0.70	0.76
		1.40	

^a References 7 and 8. ^b Reference 9. ^c Reference 11.

by Luckhurst¹¹ who suggested that three coupling constants containing 12 equivalent OCH₃ protons were sufficient to explain the spectrum. Both interpretations yield computer-simulated spectra in good agreement with the actual spectrum. Therefore an unambiguous assignment was sought by ENDOR techniques, and this was, in fact, the point of departure for this study.

Second, there is the interesting subject of molecular asymmetry in these compounds. By this we mean that the two ring protons on each ring are inequivalent and that the substituent groups on each ring are inequivalent, presumably because of "steric" interactions. Molecular asymmetry of the diamagnetic quinone methide compound found by reducing compound I has been observed by nuclear magnetic resonance (NMR).^{2,12}

In the first ENDOR experiment on galvinoxyl,⁷ the ENDOR line from the four ring protons was observed to be split, suggesting that there were two pairs of equivalent ring protons. In subsequent work,⁸ this splitting was tentatively ascribed to molecular asymmetry. Some doubt was expressed on this result in the discussion appearing at the end of ref 13, and it is now clear that this splitting is a coherence effect of considerable physical interest, but of no structural importance.¹⁴ All four ring protons of galvinoxyl are equivalent within the resolution of the ENDOR experiments. However, the ENDOR experiments described here present new evidence of molecular asymmetry in the various derivatives of galvinoxyl which does not appear related in any way to coherence and is, we believe, of structural significance.

Third, we have discovered in compound V that there are at least two isomers in solution which yield distinguishable ENDOR and EPR spectra near the freezing point of the solvent. At higher temperatures interconversion becomes sufficiently rapid that the spectral differences between the forms collapse to yield hyperfine couplings which are average values.

Fourth, we have carried out a variety of Hückel molecular orbital (HMO) calculations as modified by McLachlan.¹⁵ The difficult question in these calculations is how to treat the perturbing *t*-butyl, methoxyl, and methyl groups. Combining the theory with our experimental results, we have obtained some parameters by means of which these perturbing groups can be treated and which, we suggest, may be useful in other molecules where these groups are attached to aromatic rings.

(4) J. K. Beconsall, S. Clough, and G. Scott, *Trans. Faraday Soc.*, **56**, 459 (1960).

(5) C. Besev, A. Lund, T. Vännegård, and R. Håkansson, *Acta Chem. Scand.*, **17**, 2281 (1963).

(6) G. R. Luckhurst, *Mol. Phys.*, **11**, 205 (1966).

(7) J. S. Hyde and A. H. Maki, *J. Chem. Phys.*, **40**, 3117 (1964).

(8) J. S. Hyde, *ibid.*, **43**, 1806 (1965).

(9) C. Steelink and R. E. Hansen, *Tetrahedron Lett.*, 105 (1966).

(10) C. Steelink, unpublished results.

(11) G. R. Luckhurst, Department of Chemistry, The University of Southampton, Southampton, England, private communication.

(12) G. M. Coppinger and J. L. Jungnickel, *J. Chem. Phys.*, **38**, 2589 (1963).

(13) J. S. Hyde, *J. Phys. Chem.*, **71**, 68 (1967).

(14) J. H. Freed, D. S. Lenhart, and J. S. Hyde, *J. Chem. Phys.*, **47**, 2762 (1967).

(15) A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

Endor and Epr Experiments

Radical Preparation and Stability. Radicals III, IV, and V were prepared in toluene and radical II in dichloromethane. The solvents were degassed by freezing and pumping. In some cases they were subsequently distilled to a flask containing activated alumina, in other cases to a flask containing reagent grade PbO_2 , and in still other cases the solvents were passed through an alumina column prior to degassing. The alumina and PbO_2 are, of course, rather unspecific means for removing peroxides and water from the solvent. Approximately equal weights (using a microbalance) of activated PbO_2 and the precursor were placed in a sample tube and the solvent distilled into the tube to a concentration of the order of $10^{-3} M$ in the precursor.

Many samples were prepared in various ways over a period of several months. The initial epr intensities in these samples and the stabilities as measured by epr were not simply related to the amounts of precursor used. The samples are yellow in color, but it would appear that the dominant colored species is not the radical. Although we have been unable to isolate the variable elements in this sample preparation, we have the impression that the activated lead dioxide is particularly critical. Ours was prepared by hydrolyzing lead tetraacetate, washing in distilled water and then in acetone, and thoroughly drying (see the last section of this paper for details). Freshly activated PbO_2 worked better than that which was several months old, and reagent grade PbO_2 could not be used at all.

An interesting phenomenon was observed during the generation of radical IV. The initial epr spectrum resulting from the oxidation of IX with PbO_2 was a triplet of triplets. Upon continued shaking, IV was formed. This reaction was not observed for V.

An epr signal was obtained from compound XI, but it was almost certainly not the quinone methide compound VI. A weak seven-line spectrum corresponding to a radical concentration of about 1% of the precursor concentration was observed. The largest coupling in compounds I to V is from the single methide proton, yielding spectra with even rather than odd numbers of hyperfine lines.

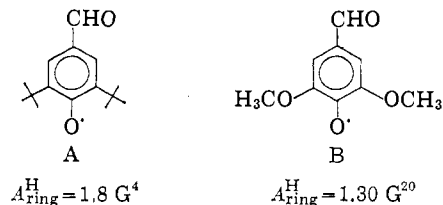
In general, replacement of *t*-butyl groups with methoxyl substituents lowers the concentration of the radical species in solution, as well as the longevity of the radicals. Presumably this is due to a greater number of possible *o*-quinone degradation products. When *t*-butyl groups are replaced by methyl groups, the radical concentrations and stabilities are even less than is the case for methoxyl substitutions. Here the known tendency for alkyl-substituted radicals to disproportionate into quinone methides is the probable cause for the instability. The approximate order of stability, as measured by the intensities of the epr signals, was: $\text{I} > \text{III} > \text{II} > \text{IV}, \text{V}$.

The Endor Technique. Since the endor technique is relatively new in the present context, it seems appropriate to review it briefly. In the endor experiment, the dc magnetic field is adjusted to one of the hyperfine lines of the spectrum, the sample is additionally exposed to a second radiofrequency magnetic field (often referred to as the nuclear radiofrequency) which corresponds approximately to the precession frequency

of the protons on the radical, and this second radiofrequency is swept. Whenever this frequency corresponds to nuclear resonance of protons which are coupled to the unpaired electron, the epr signal height is changed and an endor line results. An endor display is epr signal height *vs.* nuclear radiofrequency. Two endor lines result from each group of chemically equivalent protons, one with the applied dc magnetic field and the magnetic field from the electron at the protons parallel and one with these fields antiparallel. In the experiments described here, these two lines are equally spaced above and below the free-proton frequency. Customarily we display only half of the endor lines, sweeping from the free-proton frequency to higher frequencies. A review of endor in liquids is given in ref 16. The main motivation in performing endor is the improvement in effective resolution. One might state qualitatively that the endor resolution is one to two orders of magnitude better than ordinary epr and that the signal-to-noise ratio is one to two orders of magnitude poorer.

The first successful electron-nuclear double resonance investigation of a free radical in solution was performed on galvinoxyl.⁷ Other free radicals in solution have been investigated with endor since this first experiment.^{8, 13, 17} One result of these studies is that galvinoxyl is a particularly favorable radical from the point of view of the endor signal-to-noise ratio.

Endor of Compound II (Syrinoxyl). The endor spectrum of compound II obtained at -80° is shown in Figure 1. Commonly the endor intensity expected from a single proton decreases as the coupling becomes smaller. (This is because electron-nuclear dipolar (end) interaction which gives rise to nuclear spin-lattice relaxation is the dominant mechanism tending to restore the spin system to thermal equilibrium.^{18, 19} The endor signal height is proportional to the strength of this interaction, which in turn is proportional to the hyperfine coupling.) Since the signal heights in this spectrum *decrease* as the frequency *increases*, there can be little doubt that the line at 21.5 MHz is from the methide proton, the line at 15.3 from the four ring protons, and the line at 14.7 from the 12 methoxyl protons. This assignment is also consistent with the known assignments for compound I. Precise values for the couplings read from slow and careful scans in the immediate region of the peaks were obtained and are listed in Table II. It is clear by comparison with Table I that Luckhurst's assignment is substantially correct. The epr spectrum has been simulated on a computer using the coupling constants obtained from endor, and the agreement with the actual epr spectrum is good.



(16) J. S. Hyde in "Magnetic Resonance in Biological Systems," A. Ehrenberg, B. G. Malmström, and T. Vänngård, Ed., Pergamon Press, Oxford, 1967, p 63.

(17) J. S. Hyde, R. Breslow, and C. DeBoer, *J. Amer. Chem. Soc.*, **88**, 4763 (1966).

(18) J. H. Freed, *J. Chem. Phys.*, **43**, 2312 (1965).

(19) J. H. Freed, *J. Phys. Chem.*, **71**, 38 (1967).

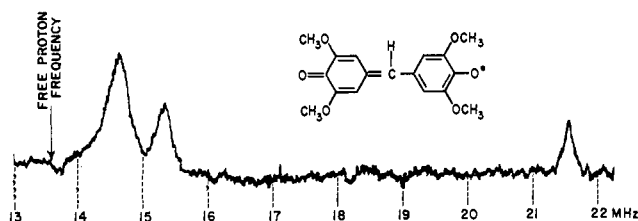


Figure 1. The endor spectrum of compound II obtained at -80° .

The decrease of the ring-proton coupling of galvinoxyl compared with syringoxyl (3.869 to 3.450 MHz) is significant. A similar effect has been observed in the monomeric species A and B as a result of methoxyl substitution for *t*-butyl.

Endor of Compound III. The endor spectrum of compound III at -80° is shown in Figure 2. The weak *t*-butyl line is seen at 13.6 MHz, and again the methide-proton line is at a high frequency: 21.2 MHz. The obvious assignment of the 15.2 and 15.6 to two pairs of ring protons and the 14.9 line to the six methoxyl protons is consistent with the results on compounds I and II and is in good agreement with the epr spectrum. In general, endor intensities are only useful as a guide in interpretation since they depend critically on relaxa-

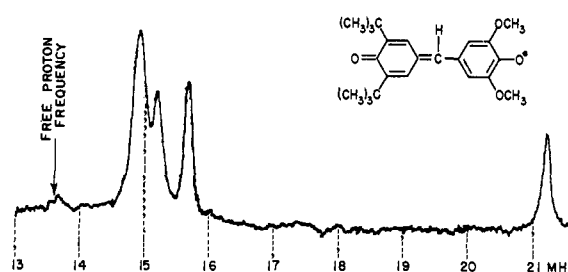


Figure 2. The endor spectrum of compound III obtained at -80° .

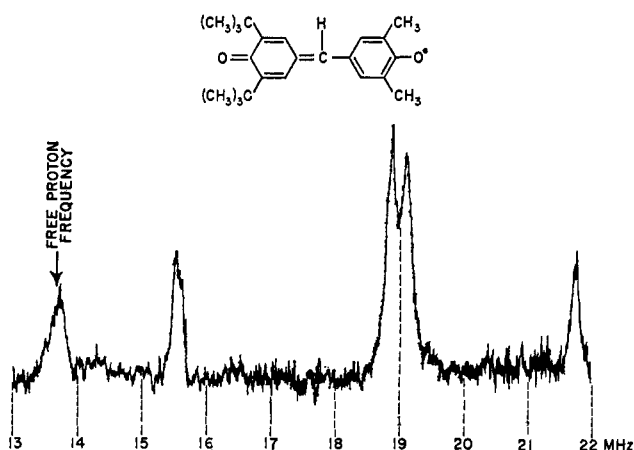


Figure 3. The endor spectrum of compound IV obtained at -80° .

Table II. Hyperfine Coupling Constants (in MHz)^a Obtained by Endor

Proton	Compound				
	I ^c	II	III	IV	V
Methide	15.591	15.968	15.136	16.22	15.14, 16.22
Ring a			4.108	3.76	3.73
Ring b	3.869 ^b	3.450	3.120		
Substituent R _{1a}			0.110	0.20	0.28
R _{2a}	0.08	2.227			11.14, 10.71
R _{1b}			2.558	10.48	
R _{2b}				10.94	0.28

^a $2 \times$ [(endor frequency in MHz) - (free proton frequency in MHz)] = $2.80 \times$ (proton coupling in gauss). ^b This is an average of the two ring coupling values given in ref 7. ^c See ref 7 and 8.

tion processes. Frequently one can make an unambiguous assignment by varying the number of protons assigned to each endor coupling until good agreement between computed and actual epr spectra is obtained. Anticipating the results of the HMO calculations, the 15.6 line is assigned to the *t*-butyl ring and the 15.2 line to the methoxyl ring. The couplings are listed in Table II.

Endor of Compound IV. The endor spectrum of compound IV at -80° is shown in Figure 3. The line at 13.6 is from the *t*-butyl protons, at 15.6 from the ring protons, and at 21.7 from the methide proton. The doublet near 19 MHz comes from the methyl groups.

The immediate question is: does the methyl splitting arise from coherence effects? These are instrumental in nature, and it has been shown¹⁴ that a splitting can be obtained of amount $\gamma_n H_2$, where γ_n is the nuclear

gyromagnetic ratio (4.2 kHz/G for protons) and H_2 is the nuclear radiofrequency field in the rotating frame. The observed splitting is 230 kHz, and we are quite sure the nuclear radiofrequency field is less than 55 G. In addition, we have observed that the splitting is independent of the nuclear radiofrequency amplitude and independent of which epr hyperfine line one is observing during the endor measurement. It seems very unlikely to us that the two methyl lines could arise from a single methyl group, and thus it is concluded that the two methyl groups are inequivalent.

The line at 15.6 has an unusual line shape resembling that found for galvinoxyl (I).^{7,8} Sometimes it shows a barely detectable splitting which we attribute to a coherence effect just as was found for galvinoxyl.¹⁴ Since the two methyl groups are believed inequivalent, this perturbation might make an additional contribution to the width and shape of the ring-proton line. Since the *t*-butyl and methyl perturbations must in principle be slightly different, this would make still another contribution to this width and shape. The surprising result is that all of these effects are so small. The couplings are listed in Table II. These values were read from Figure 3 and are less precise than values for compounds II and III.

Endor of Compound V. One of our early endor spectra from compound V obtained at -80° is shown in Figure 4. This sample gave considerable difficulty for two reasons. The radical concentration was low and somewhat unstable and unpredictable, and each time we ran the sample we obtained a different line shape for the doublet assigned to the methyl protons. Furthermore the methide-proton line in this figure is markedly lower in intensity relative to the other derivatives (Figures 1-3).

(20) C. Steelink, *J. Amer. Chem. Soc.*, **87**, 2056 (1965).

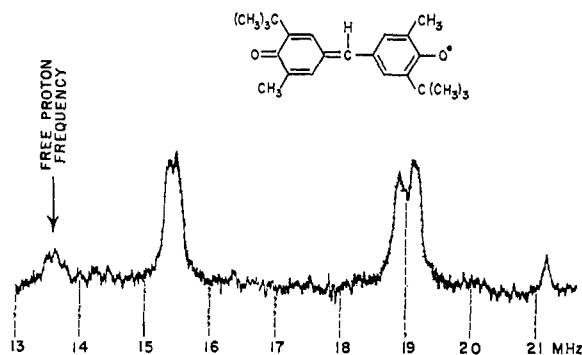


Figure 4. An early endor spectrum of compound V (see text) obtained at -80° .

It was finally realized that the line shape obtained for the methyl-proton line depended *extremely critically* on the setting of the epr resonance condition. Varying the magnetic field a small fraction of a hyperfine line width would change the endor line shape markedly. Some representative methyl lines are shown in Figure 5. By adjustment of the magnetic field, either half of the endor doublet could be made to disappear. This behavior is what one would expect if he had a mixture of two or more nearly identical radicals. Depending on where the magnetic field was set, the epr lines from the several radicals overlap differently, thus changing the endor spectra.

But if this were the proper explanation, then one might expect two or more methide-proton lines, and this might in fact be the explanation for the low methide-proton intensity in Figure 4. Searching to higher frequencies, a second methide-proton line was found. Representative spectra in this region are shown in Figure 5. By setting the magnetic field such that the higher frequency half of the methyl doublet disappears, we have observed that the lower frequency methide line disappears; when the magnetic field is such that the lower half of the methyl doublet appears only as a slight change in curvature on the low-frequency side of the higher frequency line, both methide lines are detected. In this case, however, the intensity of the lower frequency methide line is approximately twice the intensity of the higher frequency methide line.

We have attempted to detect a temperature dependence of the observed methyl splitting in this compound (as well as compound IV), but the endor signal-to-noise ratio was not sufficient for us to follow the splitting in any definitive manner. However, we have observed that the separation of the two methide lines of compound V decreases as the temperature is raised. The spectra in Figure 5 show that the confidence level in this result is not too high, but it does appear to be a real effect.

See Table II for values of all of the couplings of compound V.

Molecular Orbital Calculations and Discussion of Endor Results

Summary of the Theoretical Approach. Various HMO-McLachlan¹⁶ type calculations have been performed by us in order to understand the endor results on this series of compounds. We have used the "heteroatom model"²¹ for treating the perturbation of

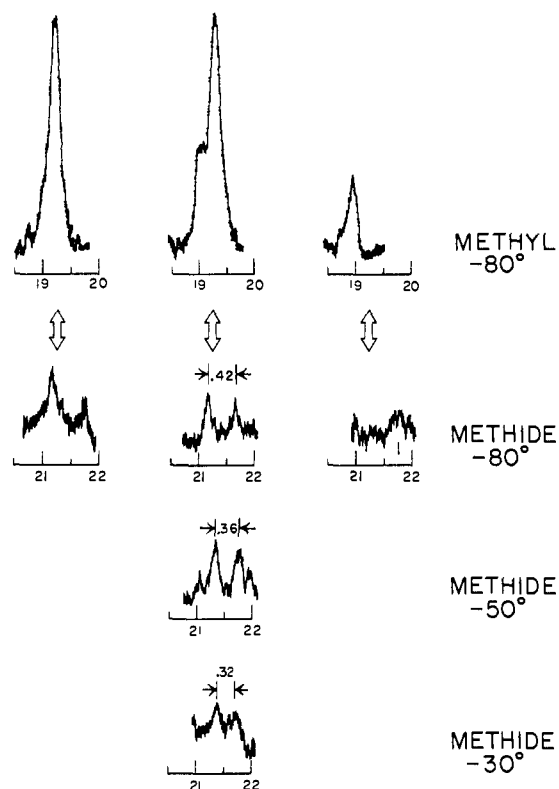


Figure 5. (First row) Methyl endor lines of compound V for different settings of the epr resonant condition. (Second row) Methide endor lines of compound V which correspond to the methyl lines of the first row. (Third and fourth rows) Methide endor lines at higher temperatures. The abscissas are in megahertz.

the spin density distribution in the benzene ring caused by the methyl, *t*-butyl, and methoxyl groups. In this model each attached group is visualized as a single electron pair on a single atom, and it is assumed that these electrons are part of the π system. Empirical parameters are introduced into the calculation which are a measure of the difference of the "heteroatom" from the benzene carbon. Thus the resonance integral between the benzene carbon C and the heteroatom X becomes $k_{C-X}\beta_0$, where β_0 is the value for two adjacent benzene carbons, and the Coulomb integral for the heteroatom is $\alpha_0 + h_X\beta_0$. Here α_0 is the benzene carbon integral and h_X is positive for an atom more electronegative than the standard carbon. Streitwieser gives $h_X = 2.0$, $k_{C-X} = 0.7$ for methyl groups.

We have used his single-bond oxygen value for the Coulomb integral, $h_O = 1$, and his double-bond value for the resonance integral, $k_{C=O} = 1$ (see p 156 of ref 21). In Table III are listed the spin densities calculated by us for galvinoxyl (I), where we have assumed that the *t*-butyl perturbations were the same as methyl perturbations.

Luckhurst⁶ has performed similar calculations on galvinoxyl, using $h_O = 1.3$ and $k_{C=O} = 1.5$. No *t*-butyl perturbation was introduced. See Table III.

The methylene-carbon spin densities in Table III are insufficient to give the observed proton hyperfine coupling. Luckhurst has suggested that this discrepancy is removed if the overlap of the methylene

(21) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 133.

Table III. Calculated Spin Densities in Galvinoxyl

	Luckhurst ^a	This work ^b
Methylene carbon	-0.0748	-0.0705
Ring proton carbons	-0.0448	-0.0364

^a 19° twist of the rings about the central C-C bonds. ^b 20° twist.

proton 1s orbital with the p orbitals on the two carbons bonded to the methylene carbon is considered. This interaction is proportional to the square of the sine of the twist angle. He finds that a twist of 19° gives the proper agreement with experiment. This angle may be somewhat low, since a Corey-Pauling-Koltun model indicates that the twist angle is about 40°.

We cite these two calculations, which were performed independently, in order to indicate to the reader the degree of uncertainty in this approach. Following Luckhurst, we have used 20° as the twist angle, but we have preferred to follow Streitwieser in treating the heteroatom perturbations.

Perturbations by the *t*-Butyl and Methoxyl Group. The endor spectrum of compound IV shows a single coupling for the four ring protons, whereas the endor spectrum of compound III shows that there are two inequivalent groups of ring protons. Thus it is concluded that *t*-butyl and methyl perturbations of the spin densities are the same and that the methoxyl perturbation differs.

We have calculated a best fit to the ring-proton couplings of compound III by varying h between 2.0 and 2.4 and k between 0.5 and 0.7. Since a methoxyl group should be more electronegative than a methyl group, it was felt that h should be somewhat higher and k somewhat lower. (Smaller values of k indicate longer bond lengths.) We find that the best fit occurs when $k_{C-X} = 0.60$ and $h_X = 2.20$. The lower ring-proton spin density is in the ring with the methoxyl groups attached. See Table II.

The fact that the ring-proton endor line of compound V shows little or no splitting is further evidence that the *t*-butyl and methyl perturbations are the same.

The Methyl Splitting of Compound IV. Corey-Pauling-Koltun models indicate that the main steric interactions are between the ring protons. There are no steric interactions in compounds II, III, and IV between the substituent groups, but with *t*-butyl groups on both rings as in compounds I and V weak interactions appear possible.

It is conceivable that the methyl splitting observed in compounds IV and V occurs because the potential in which the methyl protons rotate is altered, thus changing the average proton hyperfine interaction but not the spin density on the relevant carbons.

A second model is that the steric interaction of the ring protons perturbs the spin densities on these carbons and therefore throughout the molecule. We have performed some calculations using this second model.

Letting $h_X = 2.0$, $k_{C-X} = 0.7$ for one methyl "heteroatom" and $h_X = 2.0$, $k_{C-X} = 0.69$ for the other yields a difference in methyl couplings of 360 kHz. (The difference is assumed proportional to the observed coupling (in MHz) times the change in spin density at the relevant carbon introduced by the perturbation divided by the calculated spin density at that carbon.)

This difference is in satisfactory agreement with the observed value of 460 kHz.

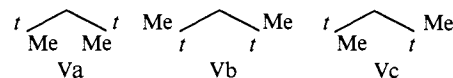
If we assume that this difference should be introduced into all five of the compounds, as is reasonable on the basis of the molecular models which indicate that the dominant steric interaction is between ring protons, we can then ask what splittings should be introduced into the various endor lines. (Note that the expected splitting of a line is one-half the difference in couplings.) The results are tabulated in Table IV.

Table IV. Calculated Splittings of Endor Lines

Compound	Proton	Splitting, kHz
I, IV, V	Ring	35
II, III	Methoxyl	40
III	Ring a	30
III	Ring b	25

Since the endor line widths are about 150 kHz, it is apparent that this predicted splitting is at best marginally detectable and obscured by coherence effects. These results are consistent with but not positive verification of the second model: that is, that steric interactions change the spin densities in the ring, rendering all six carbons on a particular ring inequivalent.

The Methyl Splitting of Compound V. One can, in principle, draw three isomers of compound V.



In this schematic representation $t = t$ -butyl and $Me =$ methyl.

If forms a and b are equally probable and form c twice as probable, then two perturbed methyls arise from compound a and two from c and two unperturbed methyls from compound b and two from c. The endor intensity from any one of these forms is approximately the product of the epr intensity of that form at the particular setting of the dc magnetic field and the number of equivalent protons giving rise to the endor line. Because the epr spectra from these forms differ, there is no single setting of the magnetic field which unambiguously gives perturbed and unperturbed methyl endor lines proportional to the total number of perturbed and unperturbed methyl groups. We have, however, reached the conclusion from a number of endor runs that the largest obtainable lower frequency methyl endor line is between one-half and one-third of the largest obtainable intensity of the higher frequency methyl line. Thus we suggest that form Vb is not populated and that two perturbed methyls come from a and two from c, with two unperturbed from c.²² The lower frequency methyl line is assigned to unperturbed methyls and the higher frequency to perturbed methyls.

The observed splitting of the perturbed and unperturbed methyl line is 230 kHz, which sets an upper limit

(22) If form c has twice the number of molecules as form a, but also more epr lines because of the inequivalence of the two methyl groups, then the largest obtainable epr signal heights from each might be about the same, depending somewhat on field-modulation amplitudes employed. On this basis, assuming form b is not allowed, the endor intensity ratio of unperturbed to perturbed methyls should be 1:3. As the inequivalence of the two methyls diminishes, this ratio would approach 1:2.

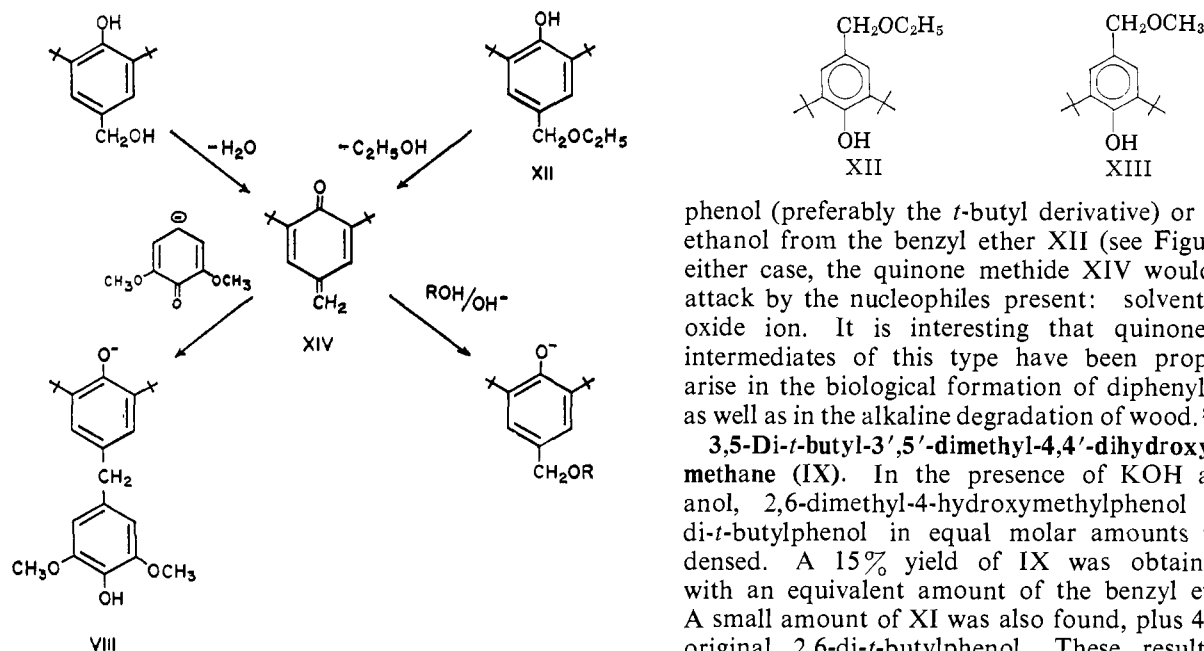


Figure 6. Proposed quinone-methide intermediate in the formation of diphenylmethanes.

at -80° for the frequency of rotation of the rings about the bond to the methylene carbon.

As previously pointed out, when the dc magnetic field is such that the ratio of the intensities of the high-frequency to low-frequency methyl endor lines increases, the lower frequency methide endor line increases in intensity relative to the higher frequency methide endor line and *vice versa*. Thus we assign the higher frequency methide coupling (16.22 MHz) to form Vc and the lower (15.14 MHz) to form Va.

We have observed that the separation of the two methide lines decreases as the temperature is raised. The signal-to-noise ratio is poor, and the endor line widths change also with temperature, but this temperature dependence appears to be real. Following the general approach of ref 17, we have obtained a very approximate activation energy of 1 kcal/mol. This number can be compared with the 5 kcal/mol attributed in ref 17 to the jumping of a triphenylmethyl derivative between left- and right-handed propeller forms.

Discussion of the Precursor Syntheses

3,5-Di-*t*-butyl-3',5'-dimethoxy-4,4'-dihydroxydiphenylmethane (VIII). The mixed dimer could not be prepared by the method used for VII, due to the insolubility of the 2,6-di-*t*-butylphenol in the aqueous alkaline solution. When ethanol was used as solvent, the 2,6-dimethoxyphenol precipitated as the sodium salt, and the products were bis-4,4'-(2,6-di-*t*-butyl-1-hydroxyphenyl)methane (galvinoxyl precursor) and XII. These two compounds accounted for almost all the original 2,6-di-*t*-butylphenol in the reaction mixture.

Optimum conditions for preparing VIII were achieved by treating XII with an excess of 2,6-dimethoxyphenol in KOH-methanol. A 65% yield of VIII was obtained; the minor constituent was identified as XIII.

The results of the various reactions strongly suggest the intervention of a quinone methide intermediate of the type XIV. This could arise by formylation of the

phenol (preferably the *t*-butyl derivative) or by loss of ethanol from the benzyl ether XII (see Figure 6). In either case, the quinone methide XIV would undergo attack by the nucleophiles present: solvent or phenoxide ion. It is interesting that quinone methide intermediates of this type have been proposed²³ to arise in the biological formation of diphenylmethanes, as well as in the alkaline degradation of wood.²⁴

3,5-Di-*t*-butyl-3',5'-dimethyl-4,4'-dihydroxydiphenylmethane (IX). In the presence of KOH and methanol, 2,6-dimethyl-4-hydroxymethylphenol and 2,5-di-*t*-butylphenol in equal molar amounts were condensed. A 15% yield of IX was obtained, along with an equivalent amount of the benzyl ether XIII. A small amount of XI was also found, plus 40% of the original 2,6-di-*t*-butylphenol. These results suggest the same mechanism as discussed above.

3,3',5,5'-Tetramethyl-4,4'-dihydroxydiphenylmethane (XI). As described above, this compound occurred as a by-product in the preparation of IX. It was also prepared by the classical method used for VII. It is quite readily air-oxidized in solution to a yellow substance; the same product occurs on melting XI. The yellow substance is not paramagnetic.

Experimental Section

4,4'-Dihydroxy-3,5,3',5'-tetramethoxydiphenylmethane (disyngylmethane) (VII) was prepared according to ref 9.

2,6-Di-*t*-butyl-4-ethoxymethylphenol (XII). 2,6-Di-*t*-butylphenol (51.5 g) was dissolved in a solution of 95% ethanol (200 ml) and 37% formaldehyde (44.6 g). A sodium hydroxide solution (10 g of NaOH in 20 ml of water) was added gradually to the cold reaction mixture under an atmosphere of nitrogen. The solution was allowed to stand 24 hr and then filtered to remove the solid, dimeric product; 3,3',5,5'-tetra-*t*-butyl-4,4'-dihydroxydiphenylmethane. The alcohol was removed from the filtrate by vacuum distillation, leaving 40.8 g of a dark viscous oil, which was distilled *in vacuo* (0.4 mm). The fraction distilling between 104 and 109° was obtained as a pale yellow oil, which set to a crystalline mass on standing. This was used without further purification.

3,5-Di-*t*-butyl-3',5'-dimethoxy-4,4'-dihydroxydiphenylmethane (VIII). 2,6-Dimethoxyphenol (30.8 g) and 2,6-di-*t*-butyl-4-ethoxymethylphenol (XII) (26.4 g) were dissolved in 300 ml of methanol in a three-necked flask, and a solution of KOH (19.8 g in 100 ml of methanol) was added gradually under an atmosphere of nitrogen. The solution was refluxed (under nitrogen) for 7 hr. After cooling and neutralizing with dilute HCl, a crystalline mass containing some KCl separated, and this was washed with 80% methanol and dried. The dried, crude product (31.4 g) was taken up in ether to remove the potassium chloride. Removal of the ether left a white crystalline solid (23.5 g) which melted at 105.5–106.5°. This was recrystallized from a mixture of ethyl ether and petroleum ether (bp 30–60°) giving 11.9 g of white crystalline material, which melted at 106–106.8° (*Anal.* Calcd for $C_{23}H_{32}O_4$: C, 74.16; H, 8.66. Found: C, 73.72; H, 8.70); ir: hydroxyl bands were found at 3665 (hindered OH) and 3575 cm^{-1} ; nmr: τ values ($CDCl_3$): 2.82 (singlet, 2 aromatic H), 3.38 (singlet, 2 aromatic H), 4.40 (singlet, 1 hydroxyl H), 4.78 (singlet, 1 hydroxyl H), 6.03 (singlet, 6 methoxyl H and 2 methylene H unresolved), and 8.45 (singlet, 18 *t*-butyl H).

(23) J. M. Harkin, *Advances in Chemistry Series*, No. 59, American Chemical Society, Washington, D. C., 1966, p 65.

(24) S. Rothenberg and P. Luner, *Advances in Chemistry Series*, No. 59, American Chemical Society, Washington, D. C., 1966, p 90.

3,5-Di-*t*-butyl-3',5'-dimethyl-4,4'-dihydroxydiphenylmethane (IX). 2,6-Di-*t*-butylphenol (16.5 g) and 2,6-dimethyl-4-hydroxymethylphenol (12.2 g) were dissolved under an atmosphere of nitrogen in 120 ml of methanol containing 9.4 g of KOH. After refluxing under nitrogen for 4 hr, the mixture was cooled and neutralized with dilute HCl. The solution was filtered to remove solid KCl, and the methanol was distilled off under reduced pressure. The oily residue was taken up in ethyl ether, washed with water, and dried over anhydrous sodium sulfate. Evaporation of the ether left 27.7 g of a brownish oil, which was distilled *in vacuo* (0.4 mm). The fraction distilling between 168 and 178° was obtained as a yellow glassy solid; yield 8.0 g. The product was purified by fractional crystallization from ligroin (bp 66–75°). A small amount of the symmetrical diphenylmethane derivative XI crystallized in the first fractions and was filtered off. Continued cooling of the ligroin caused crystallization of the desired product. After several recrystallizations from ligroin, 3.0 g of a white, crystalline solid was obtained which melted at 103° (*Anal.* Calcd for C₂₃H₃₂O₂: C, 81.13; H, 9.47. Found: C, 80.70; H, 9.40); ir: hydroxyl bands were found at 3660 (hindered OH) and 3635 cm⁻¹; nmr: τ values (CDCl₃): 2.93 (singlet, 2 aromatic H), 3.12 (singlet, 2 aromatic H), 4.92 (singlet, 1 hydroxyl H), 5.46 (singlet, 1 hydroxyl H), 6.2 (singlet, 2 methylene H), 7.78 (singlet, 6 methyl H), and 8.55 (singlet, 18 *t*-butyl H).

3,3'-Di-*t*-butyl-5,5'-dimethyl-4,4'-dihydroxydiphenylmethane (X) was prepared according to the procedure used by Kharasch and Joshi³ to prepare the diphenylmethane precursor of galvinoxyl. It was identical with the compound prepared previously by Besev, *et al.*⁵

3,3',5,5'-Tetramethyl-4,4'-dihydroxydiphenylmethane (XI). 2,6-Dimethylphenol (122.1 g) was dissolved in aqueous NaOH (50 g of NaOH and 1000 ml of water) and a 37% formaldehyde solution (178.4 g) added with stirring. After allowing the solution to

stand 3 days, it was neutralized with dilute acetic acid and cooled in an ice bath. The crystalline material which separated was filtered and washed with cold water. The product was recrystallized from aqueous ethanol solution (30% ethanol) to yield 44.7 g of a white solid, which on further recrystallization from benzene gave 34.5 g of white needles, melting at 174–176°; ir: the hydroxyl band was found at 3510 cm⁻¹ in acetonitrile solution; nmr: τ values (CDCl₃): 3.12 (singlet, 4 aromatic H), 5.48 (singlet, 2 hydroxyl H), 6.22 (singlet, 2 methylene H), and 7.72 (singlet, 12 methyl H).

The 30% ethanol solution from the above was extracted with ethyl ether, washed with water, and dried over anhydrous sodium sulfate. Removal of the ether left 77.6 g of a reddish solid, which melted at 97–101°. Recrystallization from benzene gave 66 g of white crystalline needles, with melting point 102.5–104°. The compound was identified as 2,6-dimethyl-4-hydroxymethylphenol.

Active PbO₂.²⁵ Lead tetraacetate (25 g) was stirred with 200 ml of distilled water until all was converted to brown PbO₂ (about 1 hr). The mixture was centrifuged and washed with 230-ml portions of distilled water each time, until the PbO₂ suspension was neutral to litmus. The precipitate was suspended in 25 ml of water and 13 ml of acetone added; the mixture was centrifuged. Finally, the solid was stirred four times with ethyl ether and the ether decanted. Solvent was removed in a vacuum desiccator and the PbO₂ kept overnight in the desiccator. It was finally ground in an agate mortar; yield 13.2 g.

Acknowledgments. We are indebted to Professor N. Bhacca for some of the nmr measurements. This work was supported in part by a grant from the U. S. Forest Service to C. S.

(25) R. Kuhn and I. Hammer, *Chem. Ber.*, **83**, 418 (1950).

The Thermal Rearrangements of 2-Alkenyloxypyridine 1-Oxides^{1a}

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Abstract: The thermal rearrangement of 2-alkenyloxypyridine 1-oxides has been shown to give two distinct products. At lower temperatures the product is the 1-alkenyloxy-2-pyridone which forms without a 1,3-allylic bond shift. At higher temperatures an *ortho*-Claisen rearrangement occurs to give the 3-alkenyl-1-hydroxy-2-pyridone as the major product.

Dinan and Tieckelmann showed the thermal rearrangement of 2-alkoxy-pyridine 1-oxides was facile and gave the 1-alkoxy-2-pyridone in essentially quantitative yield.² Allyl and benzyl ethers rearranged at lower temperatures than did the methyl or ethyl compounds. Since added *p*-benzoquinone did not affect the rate of rearrangement, the reactions were assumed to occur *via* an inter- or intramolecular displacement or through ion pairs.

The ease with which the 2-allyloxy- and 2-benzyl-oxypyridine 1-oxides rearrange parallels the behavior noted by Meisenheimer³ and subsequent investigators⁴ in the rearrangement of tertiary amine oxides. Because the rearrangement of *N*-crotyl-*N*-methylaniline 1-oxide

in dilute base gave *N*-methyl-*N*- α -methylallyloxylaniline, the reactions were assumed to proceed *via* an intramolecular five-membered transition state similar to that of the Claisen rearrangement.⁴

The 2-alkenyloxypyridine 1-oxide system has different geometrical requirements from the nonaromatic tertiary amine oxides studied by Meisenheimer.³ In order for a 1,3-allylic bond shift to occur, the rearrangement would have to involve a seven-membered transition state. A recent review⁵ suggests such a mechanism. This rationalization cannot be invoked as it was implied simply on the grounds that 2-allyloxypyridine 1-oxide rearranged readily at ambient temperatures. In fact, Dinan and Tieckelmann² did not propose this mechanism or that the rearrangement was similar to the *ortho*-Claisen rearrangement. In order to elucidate the reaction, we have extended the investigation to other 2-alkenyloxypyridine 1-oxides.

(1) (a) This investigation was supported by Public Health Service Research Grant No. CA-02857 from the National Cancer Institute. (b) Allied Chemical Corporation Fellow, 1966–1967.

(2) F. J. Dinan and H. Tieckelmann, *J. Org. Chem.*, **29**, 1650 (1964).

(3) J. Meisenheimer, *Ber.*, **52**, 1667 (1919); J. Meisenheimer, H. Greeske, and A. Willmersdorf, *ibid.*, **55**, 513 (1922).

(4) R. F. Kleinschmidt and A. C. Cope, *J. Amer. Chem. Soc.*, **66**, 1929 (1944); A. C. Cope and P. H. Towle, *ibid.*, **71**, 3423 (1949).

(5) B. S. Thyagarajan, *Advan. Heterocyclic Chem.*, **8**, 143 (1967).