

Electron Paramagnetic Resonance Spectra of Semiquinones.

VI. Spin and Electron Density Distributions in Bicyclo[2.2.1]heptyl and Bicyclo[2.2.2]octyl Derivatives of Semiquinone^{1,2}

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Abstract: The epr spectra of the semiquinones prepared from 3',6'-dihydroxybenzobicyclo[2.2.1]hepta-2,5-diene (1-S), 3',6'-dihydroxybenzobicyclo[2.2.1]hept-2-ene (6-S), 3',6'-dihydroxybenzobicyclo[2.2.2]octa-2,5-diene (10-S), 3',6'-dihydroxybenzobicyclo[2.2.2]oct-2-ene (13-S), and selected derivatives have been recorded and analyzed. This research reveals that the vinyl, *anti*, and *syn* protons of 1-S and 10-S are coupled, but that the bridgehead protons of these substances are not coupled perceptibly. Only the *anti* protons of 6-S and 13-S are coupled importantly. Symmetry considerations and the consequences of methyl group substitution suggest that spin density is transferred to the bicyclic fragment of the molecule without the transfer of electron density. Spin polarization, rather than electron delocalization, is apparently the important coupling mechanism in these bicyclic semiquinones.

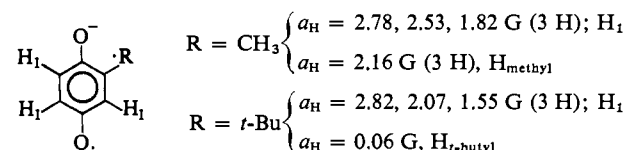
In the past 10 years, many important data concerning the distribution of spin and electron density in structurally complex neutral and charged radicals have been obtained by electron magnetic resonance spectroscopy.³ Early effort was directed toward the definition of the coupling constants for protons bonded to aromatic carbon atoms. The observations for benzosemiquinone ($a_H = 2.34$ G) and naphthosemiquinone ($a_{H_2} = a_{H_3} = 3.22$ G, $a_{H_5} = a_{H_8} = 0.67$ G, $a_{H_6} = a_{H_7} = 0.52$ G) illustrate the results that have been obtained.⁴ The, apparently correct, interpretation of the coupling of these and other aryl protons is based on the concept that spin density can be transferred without the transfer of electron density. Thus, aryl protons acquire spin density through the spin polarization of the electrons in the carbon-hydrogen bond by interaction with the electron density in the π system.⁵ McConnell pointed out that the coupling constants for such protons could be accommodated by the empirical expression

$$a_H = \rho_C^\pi Q \quad (1)$$

where Q is a constant, about -25 G, and ρ_C^π is the

electron density at the adjacent carbon atom.^{5a} The observation, $a_H = 2.34$ G, for benzosemiquinone indicates ρ_C^π is approximately 0.1. This result and the results for other aromatic compounds are in reasonable agreement with the predictions of molecular orbital treatments.^{3,4c,5b,6}

The protons of methyl groups bonded to radical centers also exhibit large coupling constants as observed for *p*-tolylsemiquinone.^{4a} Early investigators pointed out



that those couplings could arise by the transfer of electron density from the carbon-hydrogen bond to the aromatic π system *via* the overlap of the relevant orbitals, *i.e.*, hyperconjugation.^{5b,7} Subsequent work has verified the important implications of this coupling mechanism that electron transfer accompanies spin transfer and that overlap is essential.⁸⁻¹¹ Equation 2 is usually applic-

$$a_{\beta-H} = \rho_C^\pi (B_0 + B \cos^2 \theta) \quad (2)$$

able for protons in this position. The electron density in the adjacent carbon p orbital is ρ_C^π , B_0 , and B are constants near zero and 50 G, respectively, and θ is the

(1) This research was supported by the National Science Foundation, the Petroleum Research Fund, and the Biomedical Sciences Support Grant of the University of Chicago.

(2) Preliminary accounts of this work have appeared: (a) D. Kosman and L. M. Stock, *J. Am. Chem. Soc.*, **88**, 843 (1966); (b) D. Kosman and L. M. Stock, *Tetrahedron Letters*, 1511 (1967); (c) D. Kosman and L. M. Stock, *Chem. Commun.*, 551 (1968).

(3) (a) M. C. R. Symons, *Advan. Phys. Org. Chem.*, **1**, 183 (1963); (b) A. Carrington, *Quart. Rev. (London)*, **17**, 67 (1963); (c) M. Bersohn and J. C. Baird, "An Introduction to Electron Paramagnetic Resonance," W. A. Benjamin, Inc., New York, N. Y., 1966; (d) R. O. C. Norman and B. C. Gilbert, *Advan. Phys. Org. Chem.*, **5**, 53 (1967); (e) E. T. Kaiser and L. Kevan, "Radical Ions," Interscience Division, John Wiley & Sons, Inc., New York, N. Y., 1968.

(4) The results are based on data obtained for acetonitrile solution. Similar values were reported in earlier investigations: (a) B. Venkataraman, B. G. Segal, and G. K. Fraenkel, *J. Chem. Phys.*, **30**, 1006 (1959); (b) M. Adams, M. S. Blois, Jr., and R. H. Sands, *ibid.*, **28**, 774 (1958); (c) R. W. Brandon and E. A. C. Lucken, *J. Chem. Soc.*, 4273 (1961); (d) L. H. Piette, M. Okamura, G. P. Rabold, R. T. Ogata, R. E. Moore, and P. J. Scheuer, *J. Phys. Chem.*, **71**, 29 (1967).

(5) (a) H. M. McConnell, *J. Chem. Phys.*, **24**, 764 (1956); (b) R. Bersohn, *ibid.*, **24**, 1066 (1956); (c) S. I. Weissman, *ibid.*, **25**, 890 (1956).

(6) Exact agreement between theory and experiment is not realizable because solvents alter the distribution of electron density. This perturbing influence is particularly important in the semiquinone series: (a) E. W. Stone and A. H. Maki, *ibid.*, **36**, 1944 (1962); (b) J. Gendell, J. H. Freed, and G. K. Fraenkel, *ibid.*, **37**, 2832 (1962); (c) W. M. Gulick, Jr., and D. H. Geske, *J. Am. Chem. Soc.*, **88**, 4119 (1966).

(7) D. B. Chestnut, *J. Chem. Phys.*, **29**, 43 (1958).

(8) H. C. Heller and H. M. McConnell, *ibid.*, **32**, 1535 (1960).

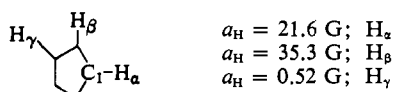
(9) (a) A. D. McLachlan, *Mol. Phys.*, **1**, 233 (1958); (b) J. R. Bolton, A. Carrington, and A. D. McLachlan, *ibid.*, **5**, 31 (1962); (c) J. A. Brivati, R. Hulme, and M. C. R. Symons, *Proc. Chem. Soc.*, 384 (1961); (d) R. Hulme and M. C. R. Symons, *ibid.*, 241 (1963).

(10) D. H. Levy and R. J. Myers, *J. Chem. Phys.*, **43**, 3063 (1965).

(11) Other aspects of the problem have been examined: (a) H. L. Strauss and G. K. Fraenkel, *ibid.*, **35**, 1738 (1961); (b) J. P. Colpa and E. de Boer, *Mol. Phys.*, **7**, 333 (1964); (c) L. M. Stock and J. Suzuki, *J. Am. Chem. Soc.*, **87**, 3909 (1965).

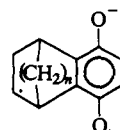
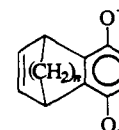
dihedral angle between the p orbital and the carbon-hydrogen bond.⁸ Though the coupling constants of β -protons are largely determined by hyperconjugation, it is apparent that the contribution of another coupling mechanism, presumably spin polarization, is not negligible.^{9a,10,11b}

These investigations have established the principal coupling mechanisms for α -protons (bonded to the radical site) and for β -protons (bonded to the adjacent carbon atom). The coupling constants for protons that are more remote from the radical center have also received some attention. The data for 2-*t*-butylsemiquinone¹² and cyclopentyl radical¹³ illustrate the usual situation



for γ -protons. For the aliphatic radical, protons H_α and H_β exhibit large coupling constants. In contrast, the constant for H_γ is very small. This small coupling has been attributed to the spin density transferred to H_γ from the p orbital centered on C_1 .^{13,14} Results of this kind indicate the merit of a localized bond model for the description of σ -bonded radicals. The data for *t*-butylsemiquinone have been interpreted somewhat differently,^{12b} but the small coupling again suggests that electron density is not importantly delocalized. A much more interesting observation is that spin density is transferred between the nonconjugated π components in the one-electron reduction products of [2.2]paracyclophane,¹⁵ derivatives of diphenylmethane and bibenzyl,¹⁶ and bis(dicyanomethylene)-2,2,4,4-tetramethylcyclobutane.¹⁷ The spectra of these radicals are consistent with equal sharing of the odd electron by the separated π systems. Rapid electron exchange between the component π systems would, of course, account for the experimental facts.¹⁸ However, the intriguing possibility that the overlap of the nonconjugated π systems is responsible for the data cannot be dismissed.^{17,19} Indeed, a molecular orbital model based on the idea that long-range π - π overlap is important and that electron density may be extensively delocalized has been advanced to account for these results.¹⁹

Long-range π - π and π - σ interactions have often been ascribed a major role in the chemistry of bicyclic molecules. The spectroscopic results discussed in the preceding paragraphs suggested that an electron magnetic resonance investigation would provide a better understanding of the interactions between the formally isolated portions of such structures. Accordingly, the spectra of saturated and unsaturated bicyclic semiquinones, I and II, were examined. Initial work²⁰ revealed that four

I, $n = 1, 2$ II, $n = 1, 2$

γ -protons of semiquinone I, $n = 2$, had an unusually large coupling constant, $a_H = 0.52 \text{ G}$. This finding prompted the additional synthetic and spectroscopic work necessary for an unambiguous interpretation of the data. The results obtained for the semiquinones are complemented by the important additional information contributed by Russell and his associates through their detailed investigations of bicyclic semidiones²¹ and by Nelsen and his coworkers through their examination of other semiquinones²² and semifuraquinones.²³ The results of these studies are compared with the observations obtained in this investigation in the following discussion.

Results

Preparation of Hydroquinones. The bicyclic and tricyclic hydroquinone derivatives were prepared from the Diels-Alder adduct of the appropriate diene and benzoquinone. Adducts of this kind have been aromatized in several ways. Diels and Alder tautomerized the adducts by a hydrogen chloride catalyzed reaction in hot acetic acid.²⁴ Reppe accomplished the same reaction thermally.²⁵ Meinwald and Wiley employed pyridine as the catalyst and carried out the reaction in the presence of acetic anhydride to obtain the diacetate of the hydroquinone.²⁶ Vaughan and Yoshimine also converted the adducts to hydroquinone diacetates but used an acid catalyst in acetic acid-acetic anhydride.²⁷ Two other procedures were devised in this investigation. In one method, the adduct was heated in a hydrocarbon solvent, e.g., heptane, with a trace of pyridine. The hydroquinone crystallized when the solution was cooled. In another method, the adduct was dissolved in aqueous ethanolic potassium hydroxide. After about 15 min, the solution was acidified with dilute aqueous hydrochloric acid to precipitate the hydroquinone. The crude product was usually acetylated and the acetate was purified prior to regeneration of the hydroquinone. Many adducts were tautomerized by more than one of these methods. In these cases, identical products were obtained indicating that rearrangements did not occur under the experimental conditions. For example, diacetates 2-D and 4-D²⁸ were prepared as described by

(12) (a) G. K. Fraenkel, *Ann. N. Y. Acad. Sci.*, **67**, 546 (1957); (b) C. Trapp, C. A. Tyson, and G. Giacometti, *J. Am. Chem. Soc.*, **90**, 1394 (1968).

(13) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

(14) (a) R. S. Drago and H. Petersen, Jr., *J. Am. Chem. Soc.*, **89**, 3978 (1967); (b) T. D. Epley and R. S. Drago, *ibid.*, **89**, 5770 (1967).

(15) S. I. Weissman, *ibid.*, **80**, 6462 (1958).

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(17) M. T. Jones, E. A. LaLancette, and R. E. Benson, *ibid.*, **41**, 401 (1964).

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(19) A. Ishitani and S. Nagakura, *Mol. Phys.*, **12**, 1 (1967).

(20) W. I. Harber, "Ninth Annual Report on Research," Petroleum Research Fund, Washington, D. C., 1964, p 56-57.

(21) (a) G. A. Russell, and K.-Y. Chang, *J. Am. Chem. Soc.*, **87**, 4381 (1965); (b) G. A. Russell, K.-Y. Chang, and C. W. Jefford, *ibid.*, **87**, 4383 (1965); (c) G. A. Russell, G. W. Holland, K.-Y. Chang, and L. H. Zalkow, *Tetrahedron Letters*, 1955 (1967); (d) G. A. Russell, G. W. Holland, and K.-Y. Chang, *J. Am. Chem. Soc.*, **89**, 6629 (1967); (e) G. A. Russell and G. R. Underwood, *J. Phys. Chem.*, **72**, 1074 (1968); (f) G. A. Russell, J. McDonnell, and C. Myers, *ibid.*, **72**, 1386 (1968).

(22) S. F. Nelsen and B. M. Trost, *Tetrahedron Letters*, 5737 (1966).

(23) S. F. Nelsen and E. D. Seppanen, *J. Am. Chem. Soc.*, **89**, 5740 (1967).

(24) O. Diels and K. Alder, *Ber.*, **62**, 2337 (1929).

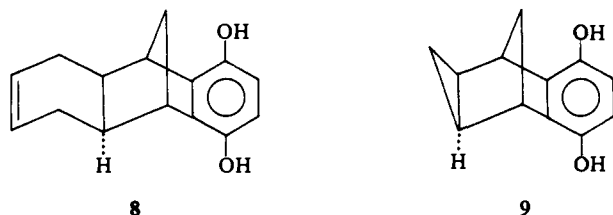
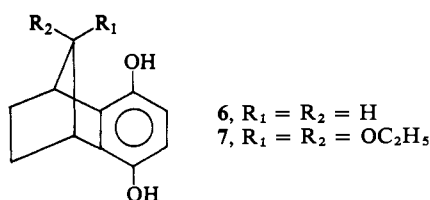
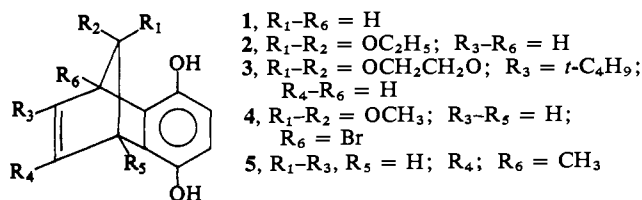
(25) W. Reppe, O. Schlichting, K. Klager, and T. Toepel, *Ann.*, **560**, 1 (1948).

(26) J. Meinwald and G. A. Wiley, *J. Am. Chem. Soc.*, **80**, 3667 (1958).

(27) W. R. Vaughan and M. Yoshimine, *J. Org. Chem.*, **22**, 7 (1957).

(28) A numeral identifies the hydroquinone, an A indicates the Diels-Alder adduct from which the hydroquinone was obtained, a D indicates the corresponding diacetate, and an S indicates the semiquinone.

Meinwald and Wiley²⁶ and by the somewhat more convenient method of Vaughan and Yoshimine.²⁷ Three precautions improved the yield and initial purity of the diacetates: first, removal of the residual benzoquinone from the adduct by recrystallization and vacuum drying (effective for the removal of the volatile quinone); second, maintenance of ice temperatures during the addition of the acid catalyst and during the early stages of the reaction; third, performance of the reaction in a nitrogen atmosphere. Ethanolic potassium hydroxide proved to be an especially useful catalyst for the tautomerization. Only this catalyst was really effective for the preparation of the tricyclic derivatives, *e.g.*, **9**.



Hydroquinone **1** was characterized by Meinwald and Wiley who also prepared the reduced compound **6-D**.²⁶ Compounds **2-4** were prepared from 5,5-diethoxycyclopentadiene,²⁹ 2-*t*-butyl-5,5-dioxadimethylenecyclopentadiene,³⁰ and 1-bromo-5,5-dimethoxycyclopentadiene,²⁹ respectively. Adduct **5-A** was prepared from 1,3-dimethylcyclopentadiene.³¹ Catalytic reduction of **2** yielded **7**. Vaughan and Yoshimine prepared **8-D**; their procedure was used.²⁷ Compound **9-D** was prepared by the cuprous bromide catalyzed decomposition of diazomethane in the presence of **1-D**. The nmr spectrum of **9-D** is consistent with an *exo* arrangement for the two methylene bridges.³²

Hydroquinone **10** was first prepared by Diels and Alder as was adduct **12-A**.²⁴ Adduct **11-A** was prepared from methylcyclohexadiene.³³ Adducts **10-A** and **11-A** were easily converted to the tautomeric diacetates, **10-D** and **11-D**. However, adduct **12-A** resisted all attempts to

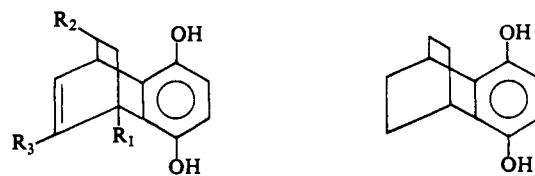
(29) P. E. Eaton and R. A. Hudson, *J. Am. Chem. Soc.*, **87**, 2769 (1965). We are indebted to Professors Eaton and Hudson for a sample of the adduct.

(30) We are indebted to Professor E. Garbisch for a sample of this diene.

(31) S. McLean and P. Haynes, *Tetrahedron*, **21**, 2313 (1965).

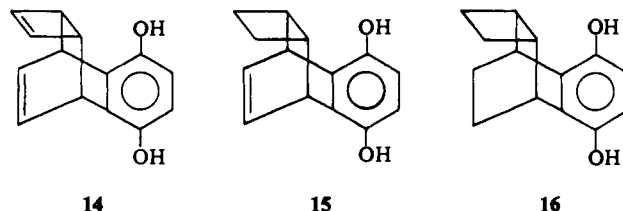
(32) M. A. Battiste and M. E. Brennan, *Tetrahedron Letters*, 5857 (1966).

(33) N. A. Domnin and V. A. Cherkasova, *Zh. Obshch. Khim.*, **26**, 1616 (1956).

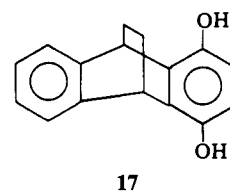


10, $R_1-R_3 = H$
11, $R_1 = CH_3$; $R_2 = R_3 = H$
12, $R_1 = H$; $R_2 = i-C_3H_7$; $R_3 = CH_3$

convert it to the diacetate or hydroquinone. Fortunately, the semiquinone could be obtained directly from the adduct. Compound **13** was obtained by the catalytic hydrogenation of **10**.



Reppe prepared **14** and **16** from cyclooctatetraene.²⁵ Nenitzescu and his associates studied the stereochemical relationship between the cyclobutane ring and the aromatic ring.³⁴ They found that the diene adduct, **14-A**, readily formed a complex with platinum chloride and pointed out that the result was good evidence for the structure shown. More recent work on the photochemistry of these adducts is in accord with this assignment.³⁵ The monounsaturated derivative, **15**, was prepared from cyclooctatriene.³⁶ Catalytic hydrogenation yielded **16**, indicating that **15**, like **14**, has the same stereochemical relationship between the cyclobutane and aromatic rings.



1,4-Dihydroxy-9,10-ethanoanthracene (**17**) was prepared from the diacetate (**17-D**) obtained by the addition of ethylene to 1,4-diacetoxyanthracene.³⁷ Several other derivatives of hydroquinone, 1,4-dihydroxy-5,8-dihydronaphthalene (**18**), 2-allyl- (**19**), 2,5-diallyl- (**20**), 2-ethyl- (**21**), 2,5-di-*n*-propylhydroquinone (**22**), and 1,4-dihydroxynaphthalene (**23**) were prepared and examined for comparison.

Spectroscopic Observations. The spectrum of semiquinone **1-S** in acetonitrile solution is typical of the results obtained in this investigation, Figure 1.

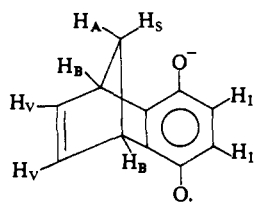
(34) (a) M. Avram, G. Mateescu, and C. D. Nenitzescu, *Ann.*, **636**, 174 (1960); (b) M. Avram, E. Sliam, and C. D. Nenitzescu, *ibid.*, **636**, 184 (1960).

(35) (a) S. Masamune, H. Cuts, and M. G. Hogben, *Tetrahedron Letters*, 1017 (1966); (b) W. G. Dauben and D. L. Whelan, *ibid.*, 3743 (1966).

(36) A. C. Cope, C. L. Stevens, and F. A. Hochstein, *J. Am. Chem. Soc.*, **72**, 2510 (1950).

(37) Y. Lepage, *Bull. Soc. Chim. France*, 1759 (1961).

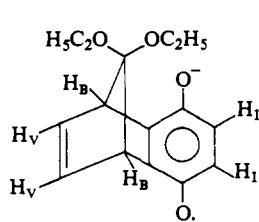
The coupling constants (similar values are reported by Nelsen and Trost²²) and their assignments for 1-S



1-S

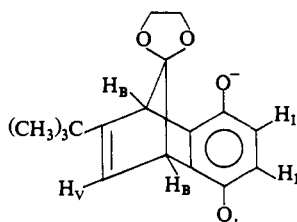
In CH ₃ CN	In C ₂ H ₅ OH
$a_H = 2.36$ G (2 H); H ₁	$a_H = 2.36$ G (2 H); H ₁
$a_H = 0.80$ G (1 H); H _A	$a_H = 0.81$ G (1 H); H _A
$a_H = 0.40$ G (3 H); H _V , H _S	$a_H = 0.50$ G (2 H); H _V
	$a_H = 0.36$ G (1 H); H _S

in acetonitrile and ethanol are shown. The data reveal that there is a modest solvent effect.⁶ The large coupling constant for 1-S, and for the other semiquinones, is rationally assigned to the aromatic protons by reference to the many prior results for alkylsemiquinones, for example, $a_H = 2.60$ G for the aromatic protons of 2,3-dimethylsemiquinone.⁴ An inspection of the data reveals that both the *syn* and *anti* protons are coupled. In addition, one other pair of protons, either the bridgehead protons or the vinyl protons, are coupled. Three group labeled derivatives, 2-S-4-S, were investigated to clarify this point. The introduction of the oxygen atoms



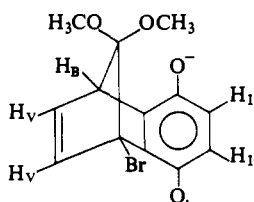
2-S

$a_H = 2.38$ G (2 H); H ₁
$a_H = 0.52$ G (2 H); H _V



3-S

$a_H = 2.48$ G (1 H); H ₁
$a_H = 2.28$ G (1 H); H ₁
$a_H = 0.52$ G (1 H); H _V



4-S

$a_H = 2.45$ G (1 H); H ₁
$a_H = 1.90$ G (1 H); H ₁
$a_H = 0.45$ G (2 H); H _V

eliminates the couplings of the *syn* and *anti* protons without altering the constants for the remaining protons significantly. The spectroscopic results for 3-S indicate that the replacement of a vinyl proton eliminates one additional proton from the coupling pattern. The results for 4-S indicate that the replacement of a bridgehead proton does not alter the coupling pattern. The spectra of these derivatives clearly indicate that the vinyl protons rather than the bridgehead protons are coupled.

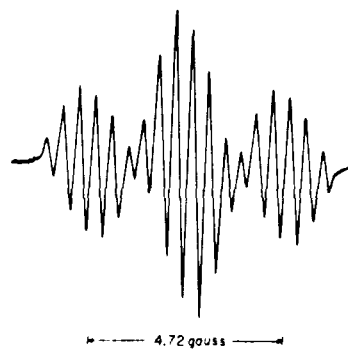
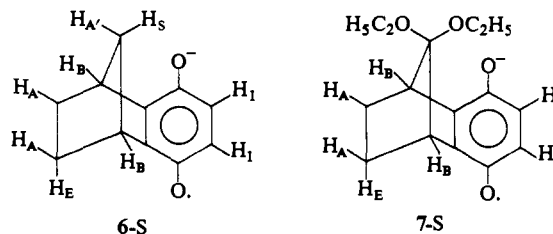


Figure 1. The epr spectrum of 1-S in acetonitrile solution at ambient temperature.

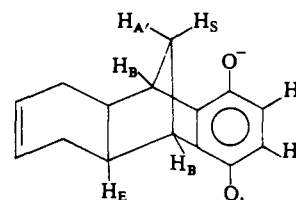
The observations for 1-S and the 7,7-disubstituted compounds show that the *syn* and *anti* protons of 1-S are coupled. However, no assignment is possible on the basis of these data alone. In a related investigation Russell and his coworkers²¹ demonstrate quite conclusively that the a_H values for *anti* protons are, in general, greater than the a_H values for *syn* protons of bicyclic semidiones. These findings suggest that $a_H = 0.80$ G should be assigned to the *anti* proton and that $a_H = 0.40$ G should be assigned to the *syn* proton. The experimental results for 6-S-8-S are in accord with this interpretation. Three protons of the bicyclic frag-



6-S

7-S

$a_H = 2.50$ G (2 H); H ₁	$a_H = 2.48$ G (2 H); H ₁
$a_H = 0.70$ G (3 H); H _A , H _{A'}	$a_H = 0.84$ G (2 H); H _A



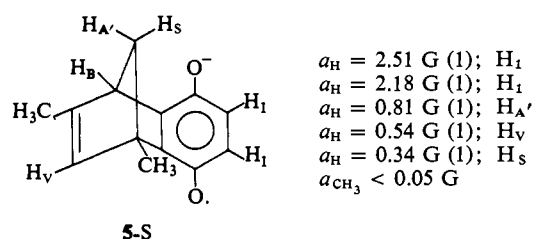
8-S

$a_H = 2.65$ G (2 H); H ₁
$a_H = 0.60$ G (1 H); H _{A'}

ment of 6-S have a large coupling constant (Nelsen and Trost report $a_{H_1} = 2.55$ G and $a_{H_A} = a_{H_{A'}} = 0.66$ G for 6-S)²² compared to two protons of 7-S and only one proton of 8-S. The identification of these three, two, and one proton couplings with the three, two, and one *anti* protons in 6-S, 7-S, and 8-S seems secure. On the basis of these observations and the data for the semidiones,²¹ the $a_H = 0.80$ G value may be assigned to the

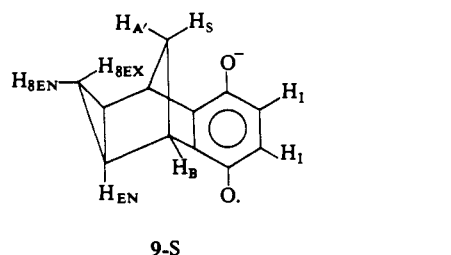
anti proton of 1-S and the remaining $a_H = 0.40$ G value must arise from the *syn* proton of 1-S.

The more complex hyperfine spectrum of 5-S yields the coupling constants shown. The two aryl protons of



5-S are coupled differently. It has been proposed that the steric desolvation of the oxygen atom *peri* to the bridgehead methyl group is responsible for a similar difference in the two coupled aryl protons of the semiquinone derived from 1-methyl-3',6'-dihydroxytryptene.^{11c} Both a bridgehead and a vinyl proton are replaced by a methyl group in 5-S. The constants for the remaining vinyl, *syn*, and *anti* protons may be assigned with confidence on the basis of the data for other bicyclic molecules (1-S-4-S). The most important feature of the spectrum of 5-S is the undetectably small coupling constant of the vinyl methyl group.

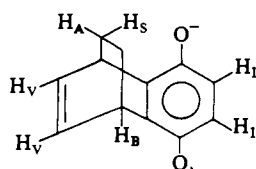
The spectrum of 9-S indicates how extensive the delocalization of spin density may be in a strained tricyclic semiquinone. Prior assignments suggest that $H_{A'}$ is



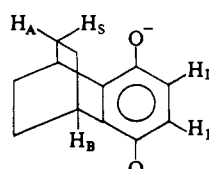
$a_H = 2.42$ G (2 H); H_1
 $a_H = 0.65$ G (1 H); $H_{A'}$
 $a_H = 0.22$ G (4 H); H_{EN}, H_S, H_{8EN} OR H_{EN}, H_S, H_{8EX}
 $a_H = 0.10$ G (2 H); H_B

responsible for the one major coupling and that H_S has an intermediate value. The smallest coupling is tentatively assigned to H_B inasmuch as the constant for these nuclei is normally below the detectable limit (between 0.05 and 0.1 G) defined by the line width. These considerations yield a coupling of 0.22 G for the *endo* protons and a coupling of 0.22 G for either H_{8EX} or H_{8EN} .

The spectroscopic observations for the bicyclo[2.2.2]octanes are summarized under structures 10-S and 13-S.

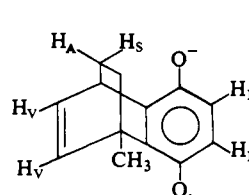


$a_H = 2.72$ G (2 H); H_1
 $a_H = 0.54$ G (4 H); H_V, H_A
 $a_H = 0.13$ G (2 H); H_S

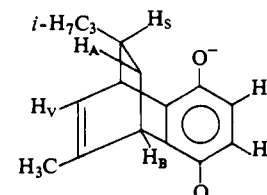


$a_H = 2.78$ G (2 H); H_1
 $a_H = 0.45$ G (4 H); H_A

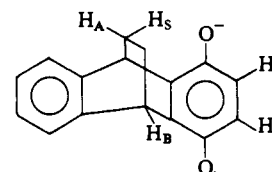
Semiquinone 10-S has four pairs of different aliphatic protons. Previous results suggest that the *anti*, *syn*, and vinyl protons are responsible for the hyperfine splittings. The coupling of the four *anti* protons of 13-S is also suggested by the previous discussion. Russell, Holland, and Chang examined 10-S, 10-S with deuterium atoms at the bridgehead positions, and 13-S in dimethyl sulfoxide solution.^{21d} The spectrum of 10-S is unchanged by the introduction of deuterium atoms proving the absence of the coupling of the bridgehead nuclei. The reported coupling constants differ only modestly from the results described here. The spectrum of 13-S in dimethyl sulfoxide is, however, more complex with the four *syn* protons ($a_H = 0.09$ G) coupled. Group-labeled derivatives were studied to verify the assignments. The observa-



$a_H = 2.66$ G (1 H); H_1
 $a_H = 2.10$ G (1 H); H_1
 $a_H = 0.57$ G (4 H); H_V, H_A

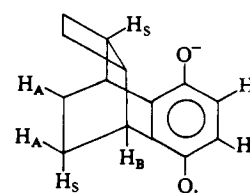


$a_H = 2.55$ G (2 H); H_1
 $a_H = 0.47$ G (2 H); H_V, H_A
 $a_{CH_3} < 0.05$ G



$a_H = 2.68$ G (2 H); H_1
 $a_H = 0.54$ G (2 H); H_A
 $a_H = 0.09$ G (2 H); H_S

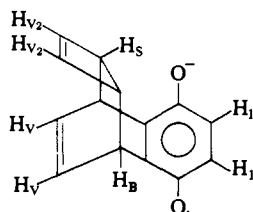
tions for 11-S, 12-S, and 17-S establish that the bridgehead protons are not coupled but that the vinyl protons are coupled. The *syn* or *anti* relationship between the isopropyl group and the aromatic nucleus in 12-S is not known with confidence (independent of the spectroscopic results which securely establish the relationship). However, the stereochemical relationship between the cyclobutane ring and the aromatic nucleus for 16-S, as already discussed, is known with certainty. Accordingly, the results for 16-S reveal that the remaining two *anti* pro-



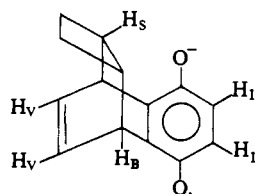
$a_H = 2.70$ G (2 H); H_1
 $a_H = 0.49$ G (2 H); H_A

tons, rather than the four *syn* protons are coupled. The group-labeled derivatives of the bicyclo[2.2.2]octane series, accordingly, confirm the assignments based on the results for the bicyclo[2.2.1]heptane series.

Two other closely related derivatives, **14-S** and **15-S**, were examined. These semiquinones were prepared to

**14-S**

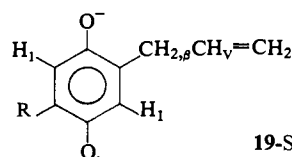
$$\begin{aligned} a_H &= 2.65 \text{ G (2 H); } H_1 \\ a_H &= 0.44 \text{ G (2 H); } H_V \\ a_H &= 0.14 \text{ G (4 H); } H_S, H_{V_2} \end{aligned}$$

**15-S**

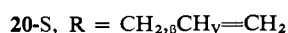
$$\begin{aligned} a_H &= 2.70 \text{ G (2 H); } H_1 \\ a_H &= 0.48 \text{ G (2 H); } H_V \\ a_H &= 0.13 \text{ G (2 H); } H_S \end{aligned}$$

establish whether the *syn* or the *anti* protons of **10-S** were coupled. That is, the results for the heptane derivatives prompted the conclusion that **14-S** and **15-S** should lack the coupling of two *anti* protons. The spectrum of **14-S** does, in fact, lack this coupling but it is more complex than expected. Three groups of 11 well-resolved lines were observed. The spacing and intensity pattern of the 11-line multiplet (1:4:6:6:9:12:9:6:6:4:1) are compatible with a large hyperfine interaction of two equivalent protons ($a_H = 0.44$ G) and a smaller hyperfine interaction with four other protons ($a_H = 0.13$ G). Similarly, the spectrum of **15-S** indicates two equivalent protons with a large constant ($a_H = 0.48$ G) and two equivalent protons with a small hyperfine constant ($a_H = 0.13$ G). The two large coupling constants may, on the basis of the results for the other bicyclic semiquinones, be assigned to the vinyl protons. The observations for the simple unsaturated molecules, **1-S** and **10-S**, reveal that the *syn* protons are coupled to a lesser degree. Accordingly, the remaining pair of couplings of **15-S** and one of the two pair for **14-S** may be reasonably assigned to the *syn* protons. The assignment of the remaining coupling in **14-S** is more speculative. However, the bridgehead proton must be close to the nodal plane of the aromatic π system. Moreover, no detectable coupling has been observed for this proton in other bicyclooctyl semiquinones. These facts suggest that the vinyl protons of the cyclobutene ring are responsible for the added coupling.

To assess the significance of the long-range interactions observed in the bicyclic and tricyclic semiquinones, other unbridged semiquinones (**18-S**–**22-S**) were

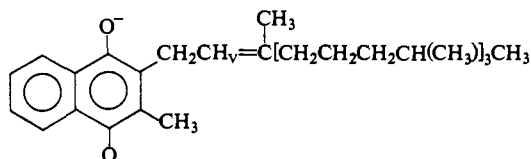
**19-S**, R = H₁

$$\begin{aligned} a_H &= 2.52, 2.47, 1.98 \text{ G (3 H); } H_1 \\ a_H &= 1.98 \text{ G (2 H); } H_\beta \\ a_H &= 0.10 \text{ G (1 H); } H_V \end{aligned}$$

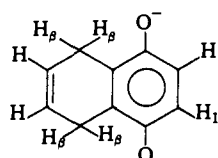


$$\begin{aligned} a_H &= 2.11 \text{ G (2 H); } H_1 \\ a_H &= 1.99 \text{ G (4 H); } H_\beta \\ a_H &= 0.12 \text{ G (2 H); } H_V \end{aligned}$$

examined. The spectra of the 2-allyl (**19-S**) and 2,5-diallyl (**20-S**) semiquinones are unexceptional except for the small coupling of the vinyl proton. The assignment of the coupling to the denoted proton is suggested by the fact that the related proton in vitamin K₁₍₂₀₎ is

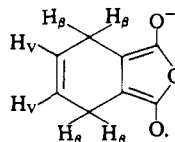


apparently coupled ($a_{H_V} = 0.05$ – 0.1 G) to the same extent.³⁸ The corresponding vinylic proton of **18-S** is not coupled perceptibly. Unfortunately, this substance

**18-S**

$$\begin{aligned} a_H &= 2.80 \text{ G (2 H); } H_1 \\ a_H &= 2.05 \text{ G (4 H); } H_\beta \end{aligned}$$

could not be examined under the conditions necessary for high resolution. The analogous semifuraquinone²⁷



$$\begin{aligned} a_H &= 6.56 \text{ G (4 H); } H_\beta \\ a_H &= 0.20 \text{ G (2 H); } H_V \end{aligned}$$

does exhibit a small coupling for this proton.

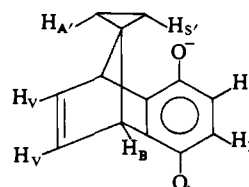
The small, $a_{H_V} \approx 0.05$ G, constant reported¹² for the nine aliphatic protons of *t*-butylsemiquinone in 50% methanol–water was readily resolved with our equipment. However, the γ -protons of the other semiquinones with saturated side chains (**21-S**, **22-S**, and 2-isopropylsemiquinone) did not exhibit detectable coupling constants in either acetonitrile or the aqueous methanol solvent.

Discussion

The coupling pattern for the saturated and unsaturated bicyclo[2.2.1]heptyl and bicyclo[2.2.2]octyl semiquinones is quite regular. The constants for the vinyl protons and the *anti* protons in these molecules are approximately equal. The coupling of the *syn* proton is detectable only when the molecule has a C₅–C₆ double bond. Bridgehead protons do not couple. Deviations from this behavior occur only in rather strained molecules such as the tricyclic semiquinone, **9-S**.³⁹ Substituents do not alter the coupling pattern importantly as shown by the sensibly equal coupling constants for the vinyl and *anti*

(38) J. M. Fritsch, S. V. Tatwawadi, and R. N. Adams, *J. Phys. Chem.*, **71**, 338 (1967).

(39) Other strained molecules also exhibit complex coupling patterns. All the protons of A have measurable coupling constants: D. Kosman and L. M. Stock, unpublished results.

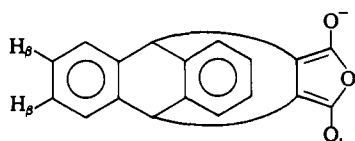


$$a_H = 2.40 \text{ G (2 H); } H_1$$

$$\left. \begin{aligned} a_H &= 0.47 \text{ G (2 H)} \\ a_H &= 0.38 \text{ G (2 H)} \end{aligned} \right\} H_V, H_A$$

$$\left. \begin{aligned} a_H &= 0.18 \text{ G (2 H)} \\ a_H &= 0.10 \text{ G (2 H)} \end{aligned} \right\} H_B, H_S$$

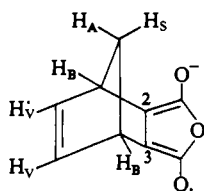
protons of the 7,7-disubstituted compounds (2-S-4-S), of the bridgehead bromide (4-S), and of the alkylated derivatives (5-S, 11-S, and 12-S). Similarly, the *anti* proton constants for the saturated compounds (6-S-8-S or 13-S and 16-S) are not altered significantly by substituents. An important feature of these data is that the protons of a methyl group bonded to the C₅-C₆ double bond do not couple measurably (5-S and 12-S). In addition, the coupling constant for the protons of an aromatic ring fused to the molecule through this double bond (17-S) is below the detectable limit. However, the four β protons of the corresponding semifuraquinone do



$$a_{\text{H}} = 0.13 \text{ G (4 H)}; \text{H}_{\beta}$$

couple.⁴⁰ Other, rather dramatic long-range couplings appear in the spectra of polycyclic radicals such as the cyclooctatetraene (14-S), cyclopropyl (9-S), and spirocyclopropane³⁹ derivatives.

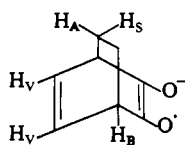
The coupling patterns for the semifuraquinones²³ are very similar. The coupling constants for the semifuraquinone related to 1-S illustrate the results.⁴¹ The larger



$$\begin{aligned} a_{\text{H}} &= 1.41 \text{ G (1 H)}; \text{H}_A \\ a_{\text{H}} &= 0.79 \text{ G (3 H)}; \text{H}_V, \text{H}_S \\ a_{\text{H}} &= 0.40 \text{ G (2 H)}; \text{H}_B \end{aligned}$$

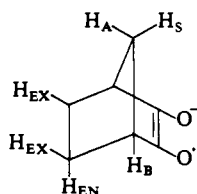
electron density on C₂ is apparently responsible for the larger coupling constants including the detectable constant for the bridgehead proton.

The coupling patterns for the semidiones²¹ and the semiquinones are not closely related. The observations for the semidione related to 10-S reveal that the vinyl



$$\begin{aligned} a_{\text{H}} &= 2.60 \text{ G (2 H)}; \text{H}_A \\ a_{\text{H}} &= 0.41 \text{ G (4 H)}; \text{H}_V, \text{H}_S \end{aligned}$$

proton coupling constant is relatively small. The results for the semidione related to 6-S show that the *anti*

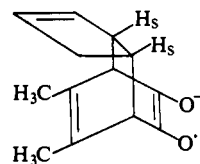


$$\begin{aligned} a_{\text{H}} &= 6.54 \text{ G (1 H)}; \text{H}_A \\ a_{\text{H}} &= 2.43 \text{ G (4 H)}; \text{H}_{\text{EX}}, \text{H}_B \\ a_{\text{H}} &= 0.41 \text{ G (1 H)}; \text{H}_S \end{aligned}$$

(40) (a) K. E. Anderson, D. Kosman, C. J. Mayers, B. P. Reukberg, and L. M. Stock, *J. Am. Chem. Soc.*, **90**, 7168 (1968); (b) T. M. McKinney, *ibid.*, **90**, 3879 (1968), reports that only four protons (unassigned) of the closely related anion radical of the dicyanoacetylene adduct of anthracene exhibit a measurable coupling constant.

(41) Observations for labeled semifuraquinones verifying these assignments have not yet been reported. The assignments are based primarily on data for related semidiones²¹ and semiquinones.^{2,22,23}

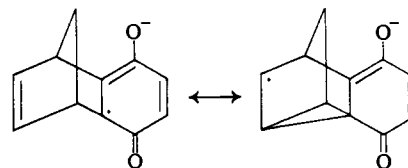
proton and the bridgehead proton coupling constants are relatively large. The near equal constants for the vinyl protons of bicyclo[2.2.2]oct-5-ene-2,3-semidione and for the protons of a methyl group bonded to the vinyl carbon atom in a related derivative^{21d} reveal another significant



$$a_{\text{H}} = 0.48 \text{ G (8 H)}; \text{H}_{\text{Me}}, \text{H}_S$$

difference. The observations for the three series of radicals, their similarities and differences, suggest the nature of the coupling mechanisms important to the delocalization of spin density.

Vinyl Proton Couplings. The coupling constants for the vinyl protons in the bicyclic semiquinones (1-S, 10-S, and their derivatives) are similar to the values for the protons of the unsubstituted ring of naphthosemiquinone⁴ and are significantly larger than the values observed for γ -protons in the allylsemiquinones (19-S and 20-S) and in the alkylsemiquinones (21-S and 22-S). Comparisons of this kind prompted the suggestion that the seemingly large constant for the vinyl proton indicated electron delocalization.^{2a} However, several alternative spin-transfer mechanisms cannot be easily dismissed. These alternatives may be grouped into two main classes—spin transfer without electron transfer to the ethylenic π bond and spin transfer with electron transfer to the ethylenic π bond.⁴² In the first category are direct (through space)^{42a} and indirect (through the σ bonds of the molecule) spin polarization of the electrons of the vinyl carbon–hydrogen bond by the spin density in the semiquinone fragment of the molecule. Electron transfer to the C₁-C₆ bond by hyperconjugation with the resultant electron density in this carbon–carbon bond leading to the spin polarization of the electrons of the vinyl carbon–hydrogen bond is another plausible mechanism. This interaction has been advanced to explain the coupling of other γ -hydrogen atoms.^{12b,21c,d} The second category includes the familiar 1,3- π - π electron transfer mechanisms. In these models proton coupling is the consequence of the spin polarization of the electrons of the vinyl carbon–hydrogen bond by electron density in the ethylenic π system. There are several ways in which electron density could be transferred to the π bond. One mechanism is the delocaliza-



tion of electron density through the overlap of the ethylenic π bond and the aromatic π system as implied in the valence bond structures. This description has received ample attention in the discussion of the electronic structures of compounds with nonadjacent π systems.⁴³

(42) (a) We have adopted Barfield's terminology for long-range proton–proton couplings to describe these electron–proton couplings: M. Barfield, *J. Chem. Phys.*, **41**, 3825 (1964); (b) Bolton^{3e} has critically discussed the fundamental features of several coupling mechanisms.

Another electron-transfer mechanism for which there is ample precedent in the chemistry of norbornadiene⁴⁴ describes the interaction as an equilibrium between the open and closed forms of the radical. A third possibility is rapid electron exchange between the otherwise isolated π systems.¹⁸

A choice between the two principal spin-transfer mechanisms can be made quite readily because they predict quite different results for the coupling constant of a methyl group bonded to the vinyl carbon atom. The mechanisms of the first category do not involve the transfer of electron density to the π bond. In this case, the spin density at the methyl group protons should be much smaller than at the vinyl proton with the constant for the vinyl proton significantly larger than the constant for the protons of the methyl group. The mechanisms of the second category, on the other hand, require that the constants for these groups be very similar inasmuch as the constants for both protons are determined by the electron density, $\rho_{C_s}^\pi$, in the adjacent π orbital. The well-known relationships, eq 1 and 2, predict a_{Me}/a_H should be unity. The experimental results for the

$$\frac{a_{Me}}{a_H} = \frac{\rho_{C_s}^\pi B \cos^2 \theta}{\rho_{C_s}^\pi Q} \approx -1 \quad (3)$$

methylated derivatives of **1-S** and **10-S**, **5-S** and **12-S**, respectively, reveal that the ratio is very small with $a_{Me} < 0.05 G$ compared to $a_H \approx 0.5 G$ for the vinyl proton. The constants for the other protons in **5-S** and **12-S** are similar to the values for the related protons in **1-S** and **10-S** indicating that the methyl group does not alter the distribution of spin density in any important way. The fact that a_{Me} is small indicates that electron density is not transferred to the ethylenic π bond. Only the coupling mechanisms of the first category are compatible with the data for the semiquinones.⁴⁵

The fact that only one vinyl proton of the allylsemiquinones, **19-S** and **20-S**, is coupled is difficult to reconcile with mechanisms involving the transfer of electron density to the isolated π bond. The result is, however, readily explained by an indirect spin-transfer mechanism. The undetectably small coupling constant for the γ -protons of the related saturated derivatives, **21-S** and **22-S**, suggests that the effective propagation mechanism

(43) (a) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley & Sons, Inc., New York, N. Y., 1962, Chapter 15; (b) L. N. Ferguson, "The Modern Structural Theory of Organic Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1963, Chapters 4 and 5.

(44) C. R. Warner, R. J. Strunk, and H. G. Kuivila, *J. Org. Chem.*, **31**, 3381 (1966), and references therein.

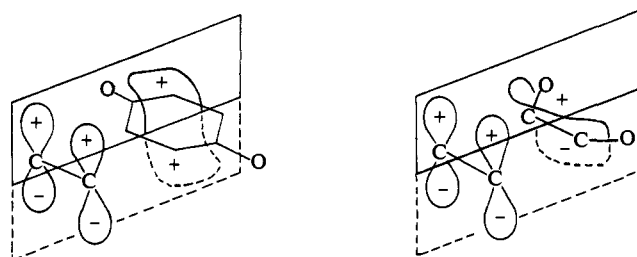
(45) A referee has disputed, "the validity of the $\cos^2 \theta$ relationship to calculate the 'allylic' spin density in the nonclassical cases. This relationship is certainly valid for simple benzylic and allylic systems but in these systems the π system containing the odd electron . . . has the best geometry (with equal electron density above and below the plane) for interaction with the allylic (or benzylic) C-H bond. . . . Nonclassical interactions in these anion radicals [may] affect the π system. If there is a change in hybridization (and thus in electron distribution in the π system) the simple hyperconjugative interactions which is generally believed to give rise to the allylic . . . coupling is drastically affected. Thus the $\cos^2 \theta$ relationship may break down."

The conclusion reached in the text is based on three confidently established points; that the ratio of a_H/a_{CH_3} for the semiquinone case is very large, that the ratio of a_H/a_{CH_3} for the semidione case is very small, and that this difference in behavior is expected on the basis of the symmetry properties of the highest occupied orbitals of the semiquinone and semidione fragments. This viewpoint is supported by the complementary observations discussed in ref 40a.

depends on the nature (hybridization) of the intervening bonds.

The spectra of the semidiones, as presented in the previous discussion, reveal that the constants for the vinyl proton and for the protons of a methyl group bonded to the vinyl carbon atom are approximately equal. This observation is, in contrast to the results for the semiquinones, readily explained by a mechanism involving the transfer of electron density to the ethylenic π bond.

The remarkable difference between the semiquinones and the semidiones may be justified theoretically. The unpaired electron in a semiquinone is in a molecular orbital which is antisymmetric with respect to a plane bisecting the quinone nucleus and the external double bond.⁴⁶ The bonding π molecular orbital of the double bond is symmetric while the antibonding π molecular orbital is antisymmetric with respect to this symmetry element. According to this perturbation model, electron donation from the double bond to the electron deficient^{3b} semiquinone nucleus is symmetry forbidden. Donation from the quinone orbital to the antibonding level of the double bond is symmetry allowed. However, the large difference in energy between the orbitals, presumably precludes a major interaction. In contrast, the unpaired electron in a semidione is in an orbital which is symmetric with respect to a plane bisecting the semidione fragment and the external double bond. The bonding π molecular orbital of the double bond is symmetric with respect to this element. In this situation, electron donation from the double bond to the semidione portion of the molecule is allowed.



No single interaction can, at the present, be identified as uniquely or dominantly responsible for the coupling of the vinyl protons in either the semiquinones or the semidiones. The data indicate that electron transfer to the ethylenic π bond is unimportant for the semiquinone. Barfield's successful explanation of long-range nuclear couplings on the basis of indirect (through bond) spin polarization prompts us to favor an interpretation of this kind.^{42a} However, neither long-range, stereospecific interactions of the kind implicit in extended Hückel theory,^{13,14,47} nor a mechanism based on electron transfer by carbon-carbon hyperconjugation with subsequent spin polarization can be completely excluded from consideration.^{12b,21c,d} The data indicate that the principal coupling mechanism for the semidiones may involve the introduction of electron density into the π bond. The electron delocalization model discussed previously^{2a,21d} is quite attractive. Again, however, the other electron-transfer mechanisms mentioned in the earlier discussion

(46) R. Bersohn, *J. Chem. Phys.*, **24**, 1066 (1956).

(47) G. R. Underwood and R. S. Givens, *J. Am. Chem. Soc.*, **90**, 3713 (1968).

cannot be excluded on the basis of the results now available. There is an additional complication. The spin-transfer mechanisms that are obviously important in the semiquinone series must also contribute to the determination of the vinyl coupling constant in the semidiones. Accordingly, the coupling constants observed for the semidione derivatives may result from both electron- and spin-transfer processes.

anti-Proton Coupling. In the semiquinones, the constants for the *anti* protons are as large as the constants for the vinyl protons. In the semidiones, the results are somewhat different with the constant for the *anti* proton substantially larger than the constant for the vinyl proton as illustrated in the data presented previously. The ethylene bridge *anti* protons and the methylene bridge *anti* protons exhibit about equal couplings in the semiquinone derivatives. In both series, the values of the constants for the *anti* protons are significantly greater than the constants for γ protons in related acyclic molecules. The structural parameters important for a large coupling are rather apparent. A W plan arrangement is necessary. This facet is shown by the greater coupling of the *anti* 7 proton compared to the *syn* 7 proton in all the bicyclic molecules. Other illustrations of this geometric requirement are found in the long-range interactions in 9-S, 14-S, and the tricyclic derivatives,³⁹ and in the related observations presented by Russell and his group.²¹ The coupling constants for the *anti* protons and for the other protons bonded to saturated carbon atoms present new problems for interpretation. No single coupling mechanism can be selected as dominant; however, the data do suggest that spin polarization (spin transfer without electron transfer) is often significant. The alternatives are discussed in the following paragraph.

Underwood and Given have recently shown that the observations for the bicyclic semidiones are compatible with the expectations of extended Hückel theory.⁴⁷ To the extent that spin polarization influences the data for the semidiones, the agreement achieved in this theoretical analysis may be illusory.⁴⁸ Other more specific interactions have been proposed in previous work. The notion that electron density could be transferred to the *anti* 7 proton by a direct interaction of the carbon-hydrogen bonding orbital and the relevant orbital of the spin label has often been considered.^{2a, b, 21c, d, 22} Indeed, the term homohyperconjugation has been suggested^{21c, d} for this interaction by analogy with homoenolization.⁴⁹ With this in mind, Russell and Whittle pointed out that the different symmetry features of the highest occupied orbitals, described in the previous section, accounted for the large constant of the *anti* 7 proton in bicyclo[2.2.1]-heptane-2,3-semidione compared to the small constant for this proton in 6-S.⁵⁰ Both direct electron transfer and direct spin transfer from the carbon-hydrogen bond orbital to the highest occupied orbital of the semiquinone may be excluded on the basis of symmetry. In addition, the spectra of 6-S and several other radicals reveal that the three *anti* protons are coupled to the same extent. This finding suggests that there is no basic difference in

the coupling mechanism for the *anti* protons of the semiquinones whether these nuclei are in, or out of the nodal symmetry plane. Clearly, an interpretation based on indirect spin polarization nicely accounts for these data, but other indirect coupling mechanisms cannot be completely excluded.

syn-Proton Couplings. When detectable, the methylene bridge and ethylene bridge *syn* protons, like the *anti* protons, of the semiquinones exhibit equal coupling constants. The striking feature of these couplings is their major enhancement by the introduction of a double bond at C₅-C₆. To illustrate, the constant for the *syn* protons of the saturated heptane, 6-S, and octane, 13-S, is not detectable.⁵¹ The constant is, in contrast, measurable in the corresponding unsaturated compounds, 1-S and 10-S. This enhancement is also observed for the *syn* protons of the semidiones²¹ and semifuraquinones.²³

It was suggested previously^{2b, 22} that the *syn* constant is enhanced by unsaturation because spin density is transferred to this proton from the C₅-C₆ π bond. The more recent finding that electron density is not transferred to this π bond negates that interpretation for the semiquinones. The *syn* 7 proton, like the *anti* 7 proton, of the heptyl semiquinones is in the nodal plane of the highest occupied molecular orbital of the semiquinone. Accordingly, all direct interactions are excluded. Indirect spin polarization offers a reasonable interpretation for these couplings. This description is preferable to an alternative based on carbon-carbon hyperconjugation because the different constants for the *syn* and *anti* protons cannot be accommodated by the hyperconjugation interaction alone. The fact that both constants increase when unsaturation is introduced at C₅-C₆ may be the consequence of the attendant change in geometry or, more plausibly, it may be the consequence of an important dependence of spin polarization on the properties of carbon-carbon bonding orbitals as mentioned in prior discussions of nuclear couplings.^{42a}

Bridgehead Proton Couplings. The constants for the bridgehead protons of the simpler saturated and unsaturated heptyl and octyl semiquinones are not detectable. However, small couplings are detectable in tricyclic derivatives such as 9-S.³⁹ Disproportionately small couplings have also been observed for bicyclo[2.2.1]heptane-2,3-semifuraquinone.²³

A discussion of these observations depends on a reliable estimate of the dihedral angle, θ , in eq 2. In the octane derivatives, this angle is 90°, and neither carbon-hydrogen hyperconjugation nor other direct mechanisms can contribute to the coupling. For the heptyl semiquinones, θ is not known with confidence because the structures of benzonorbornene and benzonorbornadiene are not established. Moreover, the structures of the bicyclic compounds that are known are very sensitive to nonbonded interactions and changes in the oxidation state of the skeletal carbon atoms.⁵² Accordingly, interpretations of the truly remarkable fact that only small bridgehead couplings are observed for the semi-

(48) This problem and the utility of the extended Hückel method and other methods are under investigation with C. Doubleday.

(49) A. Nickon, J. L. Lambert, R. O. Williams, and N. H. Werstiuk, *J. Am. Chem. Soc.*, **88**, 3354 (1966).

(50) G. A. Russell and P. R. Whittle, *ibid.*, **89**, 6781 (1967).

(51) This discussion refers to the data for acetonitrile. In dimethyl sulfoxide, a_H (*syn*) is 0.09 G for 13-S and increases to 0.18 G for 10-S.^{21d}

(52) (a) C. F. Wilcox, Jr., and C. Leung, *J. Org. Chem.*, **33**, 877 (1968); (b) J. F. Chiang, C. F. Wilcox, Jr., and S. H. Bauer, *J. Am. Chem. Soc.*, **90**, 3149 (1968).

quinones and semiquinones must be somewhat speculative. The simplest interpretation is that, contrary to the usual assignment of 65° , the dihedral angle is near 90° .⁵³ Another explanation is that the angle is about 65° as implied by molecular models and that another contribution of opposite sign, presumably, indirect spin polarization, fortuitously cancels the hyperconjugative contribution.

The bridgehead proton-coupling constants for the bicycloheptyl semidiones are normal in the sense that the data can be accommodated by eq 2 with $\theta = 65^\circ$. However, recent work has led Russell and his associates to question the simple interpretation based on carbon-hydrogen hyperconjugation.^{21f}

Long-Range Couplings. Alternative assignments for the proton couplings of **9-S** were presented in the Results. The preferred assignment, $a_H = 0.22$ G for H_{EN} , H_S , and H_{8EN} , is based on the viewpoint that the cyclopropane ring enhances the constant for the *syn* 7 proton in the same manner as a double bond and that the W plan geometry leads to the coupling of H_{8EN} . This interpretation of the spectrum of **9-S** and the previous interpretation of the spectrum of **14-S** imply that couplings may extend over four bonds. Such long-range interactions are consistent with very long-range electron-transfer mechanisms or with spin-polarization mechanisms but they are difficult to justify on the basis of hyperconjugative interactions of any form. Although there is no doubt concerning the need for W plan geometry, the strained character of the carbon-carbon bonds of these molecules also must play an important role in the propagation of spin density. The importance of this structural parameter is evident in the fact that H_{8EN} of **9-S** couples whereas the corresponding methylene proton of **8-S** does not. In addition, the *endo* protons of **9-S** are coupled. For **14-S**, the coupling of the protons of the four carbon atom ring is eliminated in the derivatives **15-S** and **16-S** which are less strained. These observations, and others, suggest that the delocalization of spin density depends on the p character of the carbon-carbon bond network over which it is propagated. Indirect spin-polarization interactions should, of course, be influenced by a factor of this kind.^{42a}

Summary and Conclusion

The results for the semiquinones indicate that the coupling mechanism for the vinyl protons does not involve the transfer of electron density to the isolated π bond. Indirect spin polarization offers a reasonable interpretation for this coupling. The same mechanism with an acknowledged dependence on the nature of the intervening bonds and the importance of W plan geometry offers an equally reasonable interpretation for the coupling of the *anti* and *syn* protons in the methylene and ethylene bridges of the bicyclic molecules. Other interactions such as those implicit in extended Hückel theory cannot be excluded; but the long-range four bond couplings mitigate against interpretations based on carbon-carbon hyperconjugation. Symmetry relationships provide a reasonable basis for the discussion of

(53) This view finds support in the structure of caldariomycin, a 3-bromobicyclo[2.2.1]heptan-2-one derivative, in which the carbon atoms of the bridgehead methyl group, the bridgehead position, the 2 position, and the ketonic oxygen atom are virtually coplanar: S. M. Johnson, I. C. Paul, K. L. Rinehart, Jr., and R. Srinivasan, *ibid.*, 90, 136 (1968).

the major difference between the semiquinones and the semidiones.

A principal objective of this investigation was to evaluate the importance of 1-3 π - π interactions *via* electron magnetic resonance. For the semiquinones, the perturbation model implies that the orbital symmetry problem overrides any potential electron delocalization effect negating an important interaction. For the semidiones, the data are compatible with modest electron delocalization with about 3% of the π electron density at the vinyl carbon atoms. Future effort must be directed toward the verification of the proposed electron delocalization mechanism through the study of the sign and magnitude of the coupling constants in other electron deficient molecules.

Experimental Section⁵⁴

3',6'-Dihydroxybicyclo[2.2.1]hepta-2,5-diene (1). Compound **1** (mp 143.5-144.5°, lit.²⁷ mp 144.0-144.5°) was prepared by the method described by Vaughan and Yoshimine²⁷ and purified by recrystallization from ethyl acetate-cyclohexane.

7,7-Diethoxy-3',6'-dihydroxybicyclo[2.2.1]hepta-2,5-diene (2). The Diels-Alder adduct²⁹ of 5,5-diethoxycyclopentadiene and benzoquinone was tautomerized to **2-D** (mp 81.0-81.5° from 60-90° petroleum ether) by the method of Meinwald and Wiley.²⁶ The diacetate was converted to **2** (mp 124.5-125.0° from 60-90° petroleum ether) with lithium aluminum hydride in the usual way.

Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.75; H, 6.87. Found: C, 68.85; H, 7.00.

3',6'-Dihydroxy-7,7-dioxadimethylenebenzo-2-*t*-butylbicyclo[2.2.1]hepta-2,5-diene (3). The ethylene ketal of 3-*t*-butylcyclopentadienone³⁰ (0.56 g, 3.1 mmol) and benzoquinone (0.22 g, 2 mmol) were dissolved in methanol (50 ml). After 12 hr at ambient temperature the solution was concentrated by the removal of methanol (about 25 ml) *in vacuo*. The adduct (yellow prisms, 0.65 g, 100%, mp 110.0-110.5°) crystallized when the solution was cooled.

Adduct **3-A** (0.50 g, 1.7 mmol) was refluxed with pyridine (2 ml) in hexane (50 ml) for 12 hr. Hydroquinone **3** (colorless prisms, mp 210° dec from 2-butanone-cyclohexane, 0.32 g) crystallized when the reaction was cooled.

Anal. Calcd for $C_{16}H_{20}O_4$: C, 69.58; H, 7.25. Found: C, 69.45; H, 7.34.

1-Bromo-7,7-dimethoxy-3',6'-dihydroxybicyclo[2.2.1]hepta-2,5-diene (4). Hydroquinone **4** (mp 181.0-181.5° from chloroform; diacetate, **4-D**, mp 147.0-148.0° from methanol) was prepared from the adduct, **4-A**²⁹ (mp 111.5-112.5° from methanol), of benzoquinone and 1-bromo-5,5-dimethoxycyclopentadiene by the method of Meinwald and Wiley.²⁶

Anal. Calcd for $C_{13}H_{13}BrO_4$: C, 49.88; H, 4.15; Br, 25.58. Found: C, 49.85; H, 4.23; Br, 25.45.

3',6'-Diacetoxybenzo-1,3-dimethylbicyclo[2.2.1]hepta-2,5-diene (5-D). Benzoquinone (2.16 g, 0.02 mol) was dissolved in methanol (50 ml) in a flask equipped with a nitrogen bubbler and a magnetic stirrer and cooled to 0°. 1,3-Dimethylcyclopentadiene³¹ (1.88 g, 0.02 mol) was added dropwise with stirring, and the mixture was allowed to stand for 18 hr, first in an ice bath and then at room temperature. The volume was reduced *in vacuo*, and the resulting yellow solid was collected and washed with a little ice-cold methanol. The mother liquor was further concentrated and a second crop collected. The combined crops were recrystallized from methanol yielding adduct **5-A** (2.0 g, 50%, mp 92-94°). A second crop of much lower purity was discarded.

Sodium hydroxide (1.2 g, 0.03 mol) was dissolved in water (10 ml) and diluted with ethanol (15 ml). Nitrogen was bubbled through the solution for 10 min and adduct **5-A** (2.0 g, 9.9 mmol) was added. The solution turned a dark reddish brown. After 15 min, concentrated hydrochloric acid (4 ml) in water (25 ml) was added with ice-bath cooling. Following the addition of more water (25 ml), the dark gummy precipitate was extracted twice

(54) All melting points are corrected. Further details concerning the methods of preparation and the spectroscopic properties of the compounds are presented by D. Kosman, "Bicyclic Semiquinones," University of Chicago Library, Chicago, Ill., 1968.

with ether (50 ml). The combined ether layers were washed twice with cold water and dried over sodium sulfate, and the solvent was removed *in vacuo*. The oil which resulted was treated with acetic anhydride (15 ml) and pyridine (5 ml) and heated on a steam bath for 5 min. After cooling and the addition of water (15 ml), the white crystalline precipitate was collected, washed with cold water, and dried. The product was sublimed (120° (0.1 mm)) and then recrystallized from methanol to yield **5-D** (mp 99.0–100.5°).

Anal. Calcd for C₁₇H₁₈O₄: C, 71.38; H, 6.40. Found: C, 71.30; H, 6.37.

3',6'-Dihydroxybenzobicyclo[2.2.1]hept-2-ene (6). Compound **1-D** was hydrogenated at low pressure over platinum to yield **6-D** (mp 121.0–122.0° from ethanol, lit.²⁶ mp 121–122°). Hydroquinone **6** (mp 172.0–173.0°) from 2-butanone–cyclohexane) was prepared from **6-D** by lithium aluminum hydride reduction.

7,7-Diethoxy-3',6'-dihydroxybenzobicyclo[2.2.1]hept-2-ene (7). Compound **2-D** was hydrogenated at low pressure over platinum to yield **7-D** (mp 98.0–99.0° from methanol). Hydroquinone **7** (mp 139.0–140.0° from 60–90° petroleum ether) was prepared from **7-D** by lithium aluminum hydride reduction.

5,8,8a,9,10,10a-Hexahydro-1,4-dihydroxy-9,10-methanoanthracene (8). Compound **8-D** (mp 117.0–118.0°, sublimed, lit.²⁷ mp 119–120°) was prepared by the addition of 1,3-butadiene to diacetate **1-D** as described by Vaughan and Yoshimine.²⁷ Hydroquinone **8** (mp 214.5–215.5° dec from benzene, lit.²⁷ mp 215.0–215.5°) was generated by the acid-catalyzed hydrolysis of this diacetate.

3',6'-Dihydroxybenzotricyclo[3.2.1.0^{2,4}]octene (9). Compound **9-D** was prepared from **1-D** by the cuprous bromide catalyzed decomposition of diazomethane as described by Pincock and Wells.⁵⁵ Diazomethane was generated *ex situ* from N-methyl-N-nitrosourea. Compound **1-D** (4.02 g, 0.015 mol) and cuprous bromide (0.50 g) in ether (75 ml) were treated with the diazomethane released from N-methyl-N-nitrosourea (9.0 g) added over 6 hr. The blackened catalyst was filtered off and the ether removed *in vacuo*. The nmr spectrum showed the residue to be a mixture of **1-D** (40%) and **9-D** (60%). This material was recrystallized from ethanol and sublimed. The reaction was repeated with the sublimate (2.75 g) and additional **1-D** (0.75 g) using cuprous bromide (1.5 g) and N-methyl-N-nitrosourea (13.0 g). The crude product contained greater than 90% **9-D** (nmr). The material was recrystallized from ethanol and sublimed to yield **9-D** (2.70 g, 60%, mp 90.0°).

Hydroquinone **9** (mp 191.0–191.5°) from benzene was prepared from **9-D** via lithium aluminum hydride reduction in the usual way.

Anal. Calcd for C₁₂H₁₂O₂: C, 76.52; H, 6.39. Found: C, 76.60; H, 6.35.

3',6'-Dihydroxybenzobicyclo[2.2.2]octa-2,5-diene (10). Compound **10** (mp 178.0–178.5° from benzene, lit.²⁴ mp 178°) was prepared as described by Diels and Alder.²⁴

3',6'-Diacetoxybenzo-1-methylbicyclo[2.2.2]octa-2,5-diene (11-D). Methylcyclohexadiene³³ (6.3 g, 0.067 mol) and benzoquinone (6.0 g, 0.056 mol) in methanol (15 ml) were heated under reflux in a nitrogen atmosphere for 1.5 hr. The adduct (mp 108–110° from methanol) was tautomerized by base, acetylated, and purified as described for **5-A** to yield **11-D** (mp 119–121°). The nmr spectrum (δ 1.75 (s) for –CH₃) indicated a pure material without a vinyl methyl group. This observation and the emr spectrum of semiquinone **11-S** identify this product as the 1-methyl derivative.

Adduct of Benzoquinone and 2-Methyl-5-isopropyl Cyclohexa-1,3-diene (12-A). Adduct **12-A** (mp 116.5–117.5° from methanol, lit.²⁴ mp 119°) was prepared as described by Diels and Alder.²⁴ All attempts to prepare the diacetate or the hydroquinone failed, but the semiquinone **12-S** could be obtained directly from the adduct.

3',6'-Dihydroxybenzobicyclo[2.2.2]oct-2-ene (13). Hydroquinone **13** (mp 212.0–212.5° from benzene) was prepared from **10** via platinum-catalyzed low-pressure hydrogenation.

anti-8',11'-Dihydroxybenzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (14). The adduct **14-A** (mp 139.0–140.0° from methanol, lit.²⁵ mp 141°) of cyclooctatetraene and benzoquinone was prepared as described by Reppe, *et al.*²⁵ This adduct was tautomerized, acetylated, and purified as for **5-A** to yield **14-D** (mp 135.0° after sublimation). Hydroquinone **14** (mp 127.5–128.5° from benzene, lit.²⁵ mp 133°) was prepared from **14-D** via lithium aluminum hydride reduction in the usual way.

anti-8',11'-Dihydroxybenzotricyclo[4.2.2.0^{2,5}]deca-7,9-diene (15). The necessary adduct was prepared in the usual way. Benzo-

quinone (6.10 g, 0.055 mol) and cyclooctatriene³⁶ (9.90 g, 0.055 mol) yielded **15-A** (6.53 g, mp 134.5–135.5° from methanol).

Adduct **15-A** (3.24 g, 0.015 mol) was tautomerized to **15-D** as described for **5-A**. The product was isolated and purified as the dihydroxy derivative rather than as the diacetate. The residue from the ether wash was recrystallized from benzene (Norit) to yield **15** (2.88 g, mp 169.5–170.5°).

anti-8',11'-Dihydroxybenzotricyclo[4.2.2.0^{2,5}]dec-7-ene (16). Compound **14** (0.42 g, 2 mmol) in ethanol (25 ml, 95%) was hydrogenated at atmospheric pressure with prerduced platinum oxide. Ninety milliliters (calculated, 88.6 ml) of hydrogen were smoothly absorbed in 100 min. The catalyst was filtered off, the solvent was evaporated *in vacuo*, and the residue was recrystallized from benzene to provide **16** (0.39 g, mp 178.0–179.0°, lit.²⁵ mp 178–180°).

The hydrogenation of **15** (0.43 g, 2 mmol) yielded **16** (mp 178.0–178.5°) which was identical in all respects with the compound prepared from **14**.

1,4-Dihydroxy-9,10-dihydro-9,10-ethanoanthracene (17). Quinizarin (1.0 g, 4.2 mmol) was added to sodium borohydride (0.32 g, 8.4 mmol) in ethanol (30 ml). After stirring for 30 min, the light-purple solution was poured into ice-water (50 ml) and then acidified with hydrochloric acid (ten drops, 10%). The solid precipitate was filtered, washed with water, and air dried. The crude quinone was treated with hot ethanol (100 ml) and filtered. Two crops of material, about 0.60 g, were obtained from the mother liquor. This material was dried and then added to pyridine (4 ml) and acetic anhydride (2 ml) at reflux. Zinc dust (0.3 g) was then added very cautiously. The mixture was stirred at reflux for 20 min and then decanted from the solids which were washed with hot acetic acid. The combined liquids were cooled and diluted with cold water (5 ml). The solid was collected and washed with water. After drying *in vacuo*, the material was recrystallized from ethanol, sublimed (140° (0.1 mm)), and recrystallized from carbon tetrachloride to yield 1,4-diacetoxyanthracene (0.40 g, mp 171.5–172.0°) as very pale yellow needles.

1,4-Diacetoxyanthracene (1.75 g, 6 mmol), hydroquinone (0.20 g), and toluene (100 ml) were treated with ethylene (cylinder pressure: 800 psi) for 72 hr at 150° (maximum pressure: 2100 psi). The solvent was removed *in vacuo*. The addition of ether to the residual oil caused it to crystallize. The ether was removed *in vacuo* and the residue was dissolved in methylene chloride, washed with dilute sodium hydroxide and water, and dried over sodium sulfate. Removal of the solvent yielded an oil which was crystallized from carbon tetrachloride to yield **17-D** (mp 152.0–152.5°, 0.86 g).

The acid-catalyzed hydrolysis of **17-D** by the method of Vaughan and Yoshimine²⁷ yielded **17** (mp 235° dec from benzene).

Anal. Calcd for C₁₆H₁₄O₂: C, 80.68; H, 6.15. Found: C, 80.75; H, 6.14.

5,8-Dihydro-1,4-dihydroxynaphthalene (18). Hydroquinone **18** (mp 210–211°, lit.²⁴ mp 212°) was prepared from benzoquinone and 1,3-butadiene as described by Diels and Alder.²⁴

2-Allylhydroquinone (19). Hydroquinone **19** (mp 91.5–92.5°, lit.⁵⁶ mp 93°) was prepared from hydroquinone monoallyl ether as described by Bell, *et al.*⁵⁶ The ether (mp 41.5–43.0°) lit.⁵⁶ mp 43°) was prepared as described by Klarman, *et al.*⁵⁷ from hydroquinone and allyl bromide in the presence of potassium carbonate.

2,5-Diallylhydroquinone (20). Hydroquinone **20** (mp 129.5–130.5° from water, lit.⁵⁸ mp 129.5–131.0°) was prepared from hydroquinone diallyl ether (mp 33–34° from ethanol, lit.⁵⁸ mp 33–34°), as described by Feiser, *et al.*⁵⁸

Ethylhydroquinone (21). Wolff-Kisher reduction of 2,5-dihydroxyacetophenone yielded hydroquinone **21** (mp 111.5–112.5° from benzene).

2,5-Di-n-propylhydroquinone (22). Hydroquinone **22** (mp 149.0–150.0° from benzene) was prepared from compound **20** via platinum-catalyzed low-pressure hydrogenation.

The spectroscopic properties of the semiquinones were recorded in the customary manner.⁴ All the spectra were simulated with a JEOLCO JRA5 system.⁵⁹

(56) A. Bell, M. B. Knowles, and C. E. Tholstrup, *Chem. Abstr.*, **48**, P11090h (1954).

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(59) We are indebted to the JEOLCO organization for the opportunity to use their equipment.

(55) R. E. Pincock and J. I. Wells, *J. Org. Chem.*, **29**, 965 (1964).