Semidiones. VI. Bicyclo[2.2.2]octane-2,3-semidione and Derivatives[1]

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Abstract: Bicyclo[2.2.2]octane-2,3-semidione and a variety of derivatives, including bicyclo[2.2.2]oct-5-ene-2,3-semidione and its benzo derivative, have been prepared and the esr spectra analyzed. Long-range hyperfine splitting by *anti*-hydrogen atoms is interpreted in terms of homohyperconjugation. Delocalization *via* 1,3-π,π overlap appears to be involved in the olefinic and benzo derivatives. When sufficiently strained a nonstereospecific delocalization of electrons to *syn*- and *anti*-hydrogen atoms can be detected, apparently *via* carbon–carbon hyperconjugation. No evidence of hyperfine splitting by hydrogen atoms at the bridgehead position (in the nodal plane of the π system) could be detected.

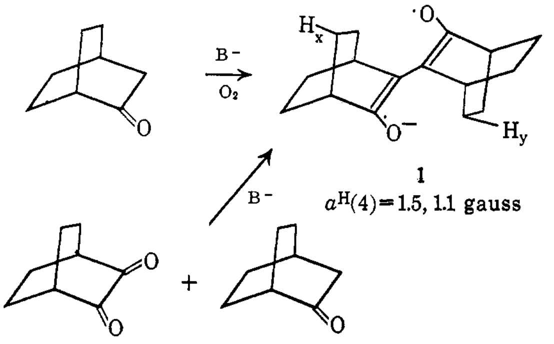
We have previously reported that a wide variety of ketones containing an α-methylene group are converted into the 1,2-semidione by treatment with traces of oxygen in dimethyl sulfoxide (DMSO) solutions containing an excess of alkali metal alkoxides[3-8] (eq A). The semidiones are produced in higher yield

$$\mathrm{RCOCH_2R' + O_2 + B^- \xrightarrow{DMSO} RC(O\cdot){=}C(O^-)R'} \qquad \text{(A)}$$

by the reduction of α-diketones, particularly by the enolate anion of propiophenone, or by the disproportionation of α-hydroxy ketones in basic solutions[9] (eq B). In the bicyclo[2.2.2]octane system a complication arises.

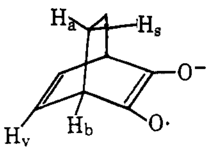
$$\mathrm{RCOCOR \xrightarrow{[C_6H_5COCHCH_3]^-}}$$
$$\mathrm{RC(O\cdot){=}C(O^-)R \xleftarrow{B^-} RCH(OH)COR} \qquad \text{(B)}$$

Oxidation of the monoketones often (but not always) forms the dimeric 1,4-semidione (**1**) which is formed in higher yield by the reaction of equal amounts of the diketone and monoketone in basic solutions. However, reduction of the α-diketone or oxidation of the α-hydroxy ketone forms the expected 1,2-semidione.



1
$a^H(4) = 1.5, 1.1$ gauss

We have investigated the hyperfine splitting of hydrogen atoms in a variety of bicyclo[2.2.2]octane derivatives that possess the structural features of **2–4**.[10] We find the strongest coupling by the *anti* hydrogens (~2 gauss in **2** and **3**, 0.5 gauss in **4**), weak or negligible coupling by the *syn* (H_a) or bridgehead (H_b) hydrogens, and moderate to weak coupling by the vinyl (H_v) or aromatic (H_{ar}) hydrogen atoms.



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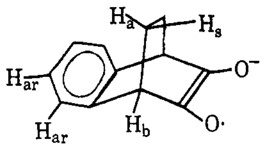

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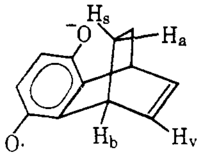
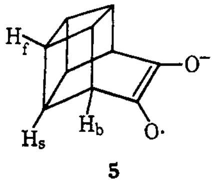


4

Saturated Bicyclo[2.2.2]octanesemidiones. Semidione **5** (prepared by reducing the corresponding diketone by propiophenone in basic DMSO) is a good model to investigate the bridgehead splitting by an α-hydrogen atom that must necessarily lie in the nodal plane of the π-electron system. The esr spectrum (Figure 1) is a sharp 1:4:6:4:1: quintet of 1:2:1 triplets. We thus assign a value of $a^H = 0.53$ gauss to H_s in **5** and $a^H = 0.09$ gauss to either H_b or H_f. A reasonable estimate of the maximum possible value of B' in the Heller–McConnell expression for hyperfine splitting of hy-



5

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[1] Application of Electron Spin Resonance Spectroscopy to Problems of Structure and Conformation. XIV. This work was supported by grants from the National Science Foundation (GP-1579, GP-6402X) and from the Petroleum Research Fund (1760-C), administered by the American Chemical Society.

[2] National Science Foundation Predoctoral Fellow, 1965–1967.

[3] G. A. Russell and E. T. Strom, *J. Am. Chem. Soc.*, **86**, 744 (1964).

[4] G. A. Russell and E. R. Talaty, *ibid.*, **86**, 5345 (1964).

[5] G. A. Russell and E. R. Talaty, *Science*, **148**, 1217 (1965).

[6] E. T. Strom, G. A. Russell, and R. D. Stephens, *J. Phys. Chem.*, **69**, 2131 (1965).

[7] G. A. Russell and K.-Y. Chang, *J. Am. Chem. Soc.*, **87**, 4381 (1965); G. A. Russell, K.-Y. Chang, and C. W. Jefford, *ibid.*, **87**, 4383 (1965).

[8] G. A. Russell, E. T. Strom, E. R. Talaty, K.-Y. Chang, R. D. Stephens, and M. C. Young, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **27**, 3 (1966).

[9] E. R. Talaty and G. A. Russell, *J. Am. Chem. Soc.*, **87**, 4867 (1965).

[10] Radical anion **4** and its saturated analog have been investigated by D. Kosman and L. M. Stock, *Tetrahedron Letters*, 1511 (1967).

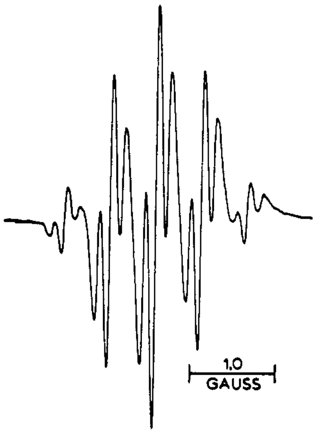


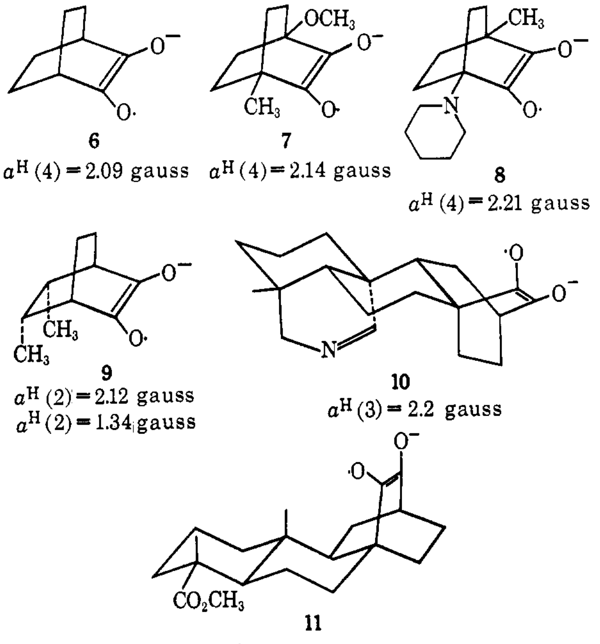
Figure 1. First derivative esr spectrum of potassium salt of **5** in dimethyl sulfoxide solution at 25°.

drogen atoms α to a site of unpaired spin density can now be made. Using ρ_{C} (the spin density at a carbonyl carbon atom in a 1,2-semidione) of about 0.25,[11] $a_{\mathrm{b}}^{\mathrm{H}}$

$$a^{\mathrm{H}} = \rho_{\mathrm{C}}(B' + B\langle\cos^2\theta\rangle)$$

= 0.09, and $\theta = 0°$ leads to a value of B' between 0.3 and 0.4 gauss. Since we feel that the 0.09-gauss splitting is actually due to $\mathrm{H_f}$ and not to $\mathrm{H_b}$, the value of B' is probably less than 0.4.[12] The low value of $a_{\mathrm{s}}^{\mathrm{H}}$ and $a_{\mathrm{b}}^{\mathrm{H}}$ in **5** is confirmed by the observed hfs of **1** and **6–11** (Chart I).

Chart I



6 $a^{\mathrm{H}}(4) = 2.09$ gauss

7 $a^{\mathrm{H}}(4) = 2.14$ gauss

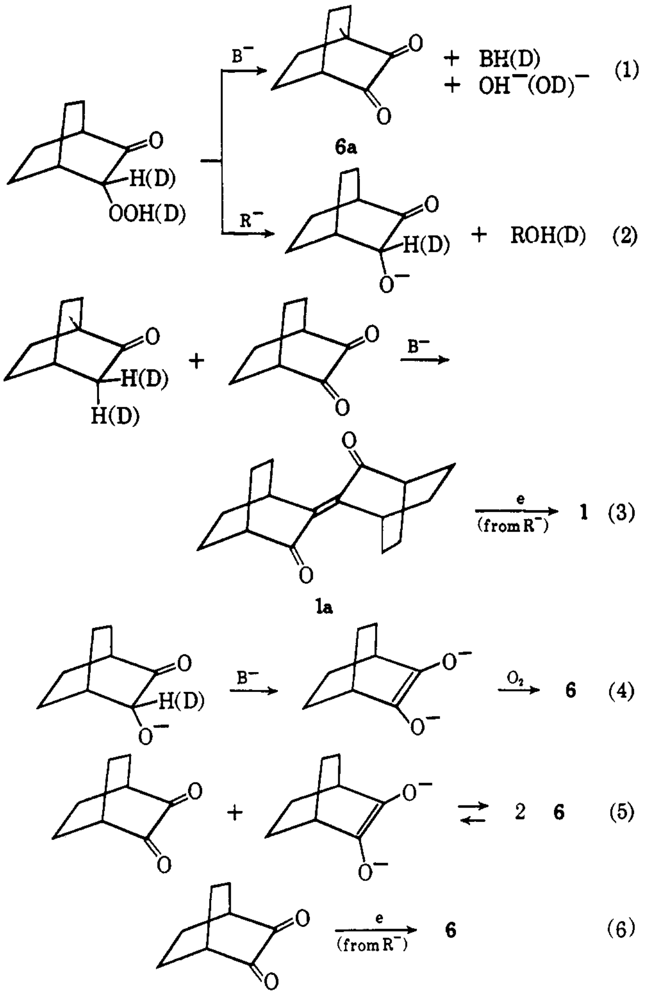
8 $a^{\mathrm{H}}(4) = 2.21$ gauss

9 $a^{\mathrm{H}}(2) = 2.12$ gauss $a^{\mathrm{H}}(2) = 1.34$ gauss

10 $a^{\mathrm{H}}(3) = 2.2$ gauss

11 $a^{\mathrm{H}}(3) = 2.3$ gauss

Semidione **6** was prepared by reduction of the diketone. Oxidation of the monoketone yielded **1** as did reaction of mixtures of the monoketone and diketone with base. Continued exposure of **1** to oxygen in basic solution led to the production of **6**. Surprisingly **6** can be prepared in DMSO-d_6 by oxidation of the monoketone. The solvent effect can be qualitatively explained as arising by isotope effects in the decomposition reactions of an initially formed keto hydroperoxide and in the condensation reactions given in eq 1–7.



$$1 + 6a \rightleftharpoons 6 + 1a \qquad (7)$$

We might expect an isotope effect of severalfold in both reactions **1** and **3**. Apparently decreasing the rate of formation of **1a** by about tenfold changes the predominant paramagnetic product from **1** to **6**. We have provided other examples of the formation of dimeric semidiones in the steroidal 17-ketones containing a *trans* C/D ring fusion.[13] The occurrence of this side reaction, once recognized and documented, presents no problem in our spectral assignments since the hyperfine splitting patterns of the dimeric and monomeric semidiones are quite different. Figure 2 presents the observed spectra from oxidation of bicyclo[2.2.2]-octan-2-one in DMSO (semidione **1**) and in DMSO-d_6 (semidione **6**).

Identical spectra of semidione **6** are obtained from the diketone in DMSO or in DMSO-d_6. Semidiones **7**, **8**, **9**, and **11** could be prepared by the oxidation of the monoketones. The same spectra were observed after oxidation of the monoketones in DMSO or DMSO-d_6. Attempts to prepare **10** from the monoketone (carbonyl

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(11) G. A. Russell, E. T. Strom, E. R. Talaty, and S. A. Weiner, *J. Am. Chem. Soc.*, **88**, 1998 (1966).

(12) Among other estimates of B′ are 1.1 gauss [J. P. Colpa and E. de Boer, *Mol. Phys.*, 7, 333 (1963)], 3–4 gauss [A. Horsfield, J. R. Morton, and D. H. Whiffen, *ibid.*, **5**, 115 (1962)], and 4.5 gauss [S. Ogawa and R. Fessenden, *J. Chem. Phys.*, **41**, 994 (1964)]. The problem in estimating B′, from the Heller–McConnell expression when applied to a flexible system, even when the equilibrium dihedral angle (θ) is known, has been discussed by E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **37**, 1326 (1962).

(13) G. A. Russell, E. R. Talaty, and R. Horrocks, *J. Org. Chem.*, **32**, 353 (1967).

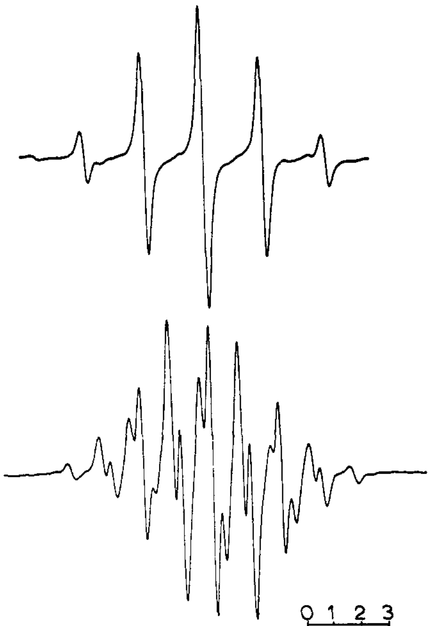
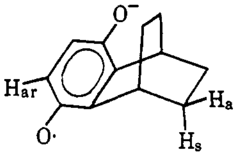


Figure 2. First derivative esr spectra of potassium salts of **6** (top) and **1** (bottom) in dimethyl sulfoxide solution at 25°.

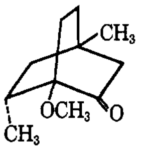
next to unsubstituted bridgehead) led to the dimeric semidione analogous to **1**, a^{H} (six equivalent hydrogens = 1.45 gauss). The monomeric semidione was prepared by oxidation of either the monoketone in DMSO-d_6 or the α-hydroxy ketone in DMSO. Spectra observed for **9** and **11** are given in Figures 3 and 4.

The only combination of hfsc that will provide a consistent interpretation to the spectra of **1** and **6–9** is that $a_{\text{bridgehead}}^{\text{H}}$, $a_{syn}^{\text{H}} \cong 0$, and $a_{anti}^{\text{H}} \gg 0$. In **9** *anti*-methine hydrogens interact much more weakly (1.34 gauss) than the *anti*-methylene hydrogens (2.12 gauss). The spectrum of **10** is consistent with this interpretation. However, the spectrum of **11** was somewhat surprising since now the *anti*-methine hydrogen atom is not seen. With these results in mind it is now possible to assign the hfsc in **12**[14] and structure to **13**. Compound **13** produced a semidione with hfs by three hydrogen atoms (2.1 gauss) and a single hydrogen atom of 0.93 gauss. On the basis of the esr spectrum, ketone **13**, prepared by a cyclization reaction,[15] must have the methyl group *syn* to the carbonyl group.



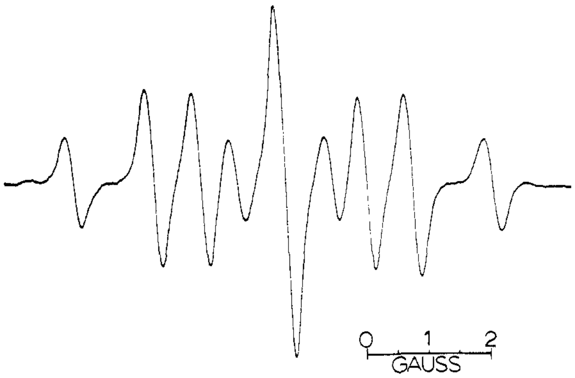
12

a_{ar}^{H} (2) = 2.67
a_{a}^{H} (4) = 0.40
a_{s}^{H} (4) = 0.09



13

In the semidione derived from **13** we notice a large effect of the bridgehead methoxy and the *syn*-methyl group on the value of the hfsc for the *anti*-methine hydrogen atom. Apparently this is the same effect observed in semidione **11** and to a lesser extent in **9**. These observations lead us to suggest that the mechanism of the long-range interaction responsible for the large value of a_{anti}^{H} in the bicyclo[2.2.2]octanesemidiones is due to a conjugation effect which we shall refer to as homohyperconjugation.[16] This effect is obviously analogous to homoenolization.[17] Introduction of carbon–carbon or carbon–oxygen bonds at the bridgehead and *syn* positions apparently greatly decreases the contribution of structure **14**, perhaps by destabilization of **14** by steric considerations or perhaps by a greater repulsion of the electron pairs in the carbon–carbon bonds (relative to carbon–hydrogen bonds) to the unpaired electron in the semidione. The contribution of structure **14** can be easily calculated. A free hydrogen atom has an hfsc of 508 gauss. The value of a_{anti}^{H} observed in **6** is thus consistent with 2.1/508 = 0.004 of an unpaired spin per hydrogen. Since the spin density at the carbonyl carbon atom in **6** is about 0.25, structure **14** represents a delocalization of about 1.5% of this spin density. The four equivalent structures **14** represent a total delocalization of 3% of the unpaired spin density of the carbonyl carbon atoms. In **1** the relative spin densities on the carbonyl



Figre 3. First derivative esr spectrum of potassium salt of **9** in dimethyl sulfoxide solution.

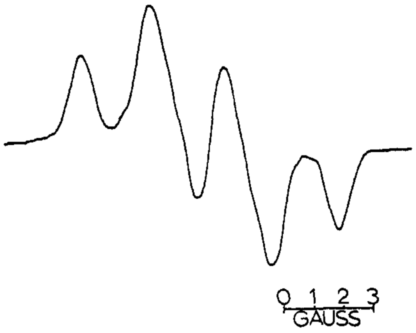
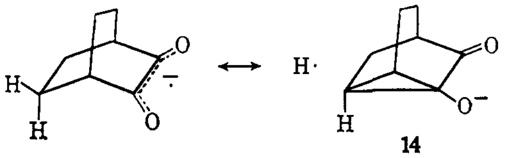


Figure 4. First derivative esr spectrum of potassium salt of **11**.



14

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[14] Hyperfine splitting constants of 2.78 (2) and 0.45 (4) have been reported for **12** in acetonitrile solution.[10]

[15] K. Morita, M. Nishimura, and Z. Suzuki, *J. Org. Chem.*, **30**, 533 (1965).

[16] G. A. Russell, G. W. Holland, K.-Y. Chang, and L. H. Zalkow, *Tetrahedron Letters*, 1955 (1967).

[17] A. Nickon and J. L. Lambert, *J. Am. Chem. Soc.*, **84**, 4604 (1962); **88**, 1905 (1966); A. Nickon, J. H. Hammans, J. L. Lambert, and R. O. Williams, *ibid.*, **85**, 3713 (1963); A. Nickon, J. L. Lambert, R. O. Williams, and N. H. Werstink, *ibid.*, **88**, 3354 (1966).

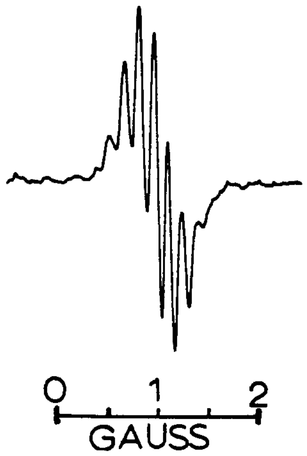
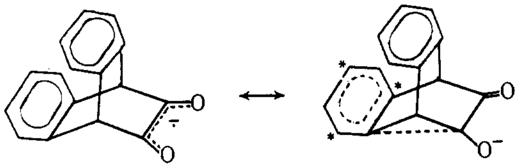


Figure 5. First derivative esr spectrum of potassium salt of radical anion **17** in dimethyl sulfoxide solution.

and vinyl carbon atoms can be estimated in the π system to be about 0.18 ($a_x^{H} = 1.5$ gauss) and 0.13 ($a_y^{H} = 1.1$ gauss).[18] In **12** the spin densities on the *ortho* aromatic carbon atoms can be estimated. From $a_{ar}^{H} = 2.67$ and $a^{H} = 23\rho_C$, it is calculated that $\rho_C = 0.11$. From $a_{anti}^{H} = 0.40$ gauss and assuming exactly the same extent of delocalization in **12** and **6**, ρ_C is calculated to be 0.05.[18] Perhaps the geometry of **12** is sufficiently different from **6** so that less homohyperconjugation occurrs in **12** than in **6** for a normalized carbon spin density.

Unsaturated Bicyclo[2.2.2]octanesemidiones. Semidiones **15**–**20** were prepared by reduction of the diketones in DMSO solution by the anion of propiophenone. The semiquinones **21** and **22** were also prepared by treatment of the hydroquinone diacetates with potassium *t*-butoxide in DMSO (Chart II).

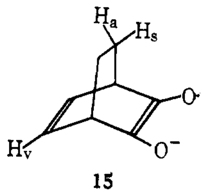
The approximate magnitude of spin delocalization into a benzosubstituent is given by **17** (Figure 5) in which eight equivalent (or nearly equivalent) hydrogen atoms are observed.[19] In benzene radical anion the value of ρ_C is of course $^1/_6$ and $a^{H} = 4$ gauss. It follows that in **17**, $\rho_{C\text{-aromatic}}$ is 0.006. Thus structure **23** involves delocalization of 0.018 of spin density. Since the carbonyl carbon atom possesses about 0.25 of an unpaired spin, this delocalization represents 7% of the spin. The four equivalent structures of type **23** represent a total delocalization of 14% of the unpaired spin density on the two carbonyl carbon atoms of **17**.[20]



23

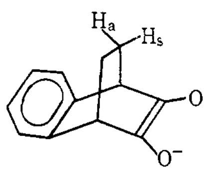
---, π overlap

Chart II



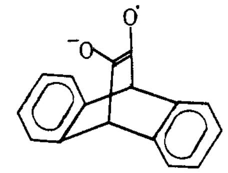
15

a^{H} (2) = 2.60
a^{H} (4) = 0.41



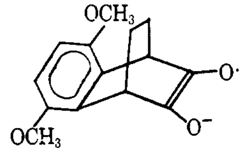
16

a^{H} (2) = 2.35
a^{H} (2) = 0.20
a^{H} (4) = 0.09



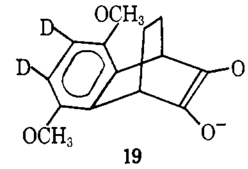
17

a^{H} (8) = 0.15



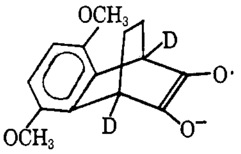
18

a^{H} (2) = 2.28
a^{H} (2) = 0.29



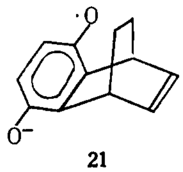
19

a^{H} (2) = 2.32
a^{H} (2) = 0.28



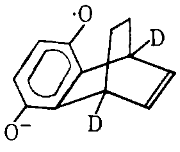
20

a^{H} (2) = 2.39
a^{H} (2) = 0.29



21

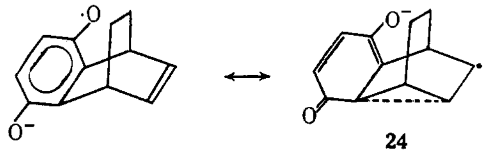
a^{H} (2) = 2.62
a^{H} (4) = 0.49
a^{H} (2) = 0.18



22

a^{H} (2) = 2.62
a^{H} (4) = 0.49
a^{H} (2) = 0.18

In **18**, **19**, and **20** this delocalization was not detected (<0.15 gauss) but in addition to a_{anti}^{H} (~2.3 gauss) we found $a_{syn}^{H} = 0.28$ gauss. The similarity of hyperfine splitting of **21** and **22** with **18**–**20** suggest the following hfs assignment for **21**: $a_{ar}^{H} = 2.62$, $a_{anti}^{H} = 0.49$, $a_{vinyl}^{H} = 0.49$, $a_{syn}^{H} = 0.18$ gauss. The value of ρ_C for the *ortho* atoms in **21** is calculated to be 0.105 from a_{ar}^{H} and 0.06 from the values of a_{anti}^{H} (assuming **6** can be used as a model). Finally, $\rho_{vinyl\text{-}C}$ in **21** can be taken as 0.49/23 = 0.021 for this trigonal atom. The two equivalent structures **24** involve the delocalization of about 4% of the total unpaired spin of **21** and about 100(0.04/2(0.06)) = 30% of the spin density on the two approprirate *ortho* positions in the semiquinone structure.



24

—, 1,3 π overlap

In **15** it seems assured that $a_{anti}^{H} = 2.60$ gauss and $a_{vinyl}^{H} = 0.41$ gauss. This leads to a delocalization *via* the two equivalent structures **25** of 0.036 spin density, or approximately 7% of the total carbonyl carbon spin density. In addition 2% of the total carbonyl

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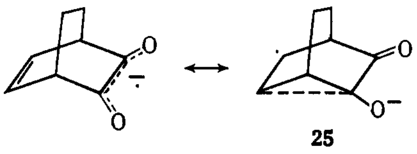
[18] From the relationship 2.1/0.25 = 1.5/0.18 = 1.1/0.13 = 0.40/0.05.

[19] The spectrum previously attributed to **17**[7,8] is actually due to anthracene-9,10-semiquinone. The quinone is a common impurity in preparations of dibenzobicyclo[2.2.2]octadiene-2,3-dione. Our original report on this semidione employed a sample, reportedly of the dione, which we did not synthesize or examine for purity, and which was actually 9,10-anthracenequinone by melting point, mixture melting point, and nmr and mass spectra.

[20] This type of delocalization was originally suggested by D. Kosman and L. M. Stock, *J. Am. Chem. Soc.*, **88**, 843 (1966). These workers found a^{H} = 2.72 (2), 0.54 (4), and 0.13 (2) for **21**.[10]

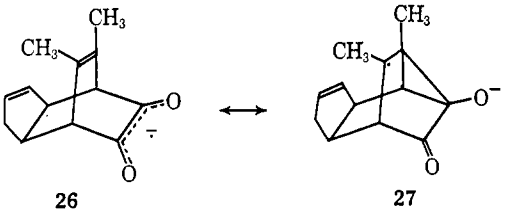


25

···1, 3 π overlap

carbon spin density is delocalized *via* the two equivalent structures of type **14**.

Semidione **26**, prepared by reduction of the diketone,



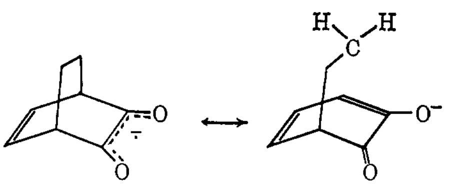
26 **27**

gave a spectrum of nine lines separated by 0.48 gauss. It appears that the two methyl groups and the two *syn* hydrogens are involved and that all the hfsc are nearly equivalent. The magnitude of delocalization by structure **27** can be estimated from the equation[10] $a_{\mathrm{CH_3}}{}^{\mathrm{H}} = 20\rho_{\mathrm{CCH_3}}{}^{\pi}$. This leads to $\rho_{\mathrm{CCH_2}}{}^{\pi} = 0.024$ or a contribution to **27** to the total resonance hybrid of 2.4%. Total delocalization of the carbonyl carbon unpaired spin density by the two structures of type **27** would be $2(2.4/0.5) \cong 10\%$.

In **18–22** hfs by *syn*-hydrogen atoms was observed but bridgehead splitting could not be resolved. Presumably the two *syn*-hydrogen atoms in **15** undergo hfs with $a^{\mathrm{H}} = 0.41$ gauss, about the same order of magnitude as observed in **5**. The most reasonable assignment in **16** is $a_{anti}{}^{\mathrm{H}} = 2.35$, $a_{syn}{}^{\mathrm{H}} = 0.20$, $a_{\mathrm{ar}}{}^{\mathrm{H}} = 0.09$ gauss.

Discussion

Upon inspection of the variation in $a_{syn}{}^{\mathrm{H}}$ and $a_{anti}{}^{\mathrm{H}}$ for the various semidiones in the bicyclo[2.2.2]octane system, it becomes apparent that $a_{anti}{}^{\mathrm{H}} - a_{syn}{}^{\mathrm{H}}$ is relatively constant. For **6–11** $a_{syn}{}^{\mathrm{H}}$ is not observed and is probably <0.10 gauss. The value of $a_{anti}{}^{\mathrm{H}} - a_{syn}{}^{\mathrm{H}}$ is thus 2.0–2.2 gauss. For **15** the difference is 2.60 − 0.41 = 2.2. For **16** the difference is 2.15 while for **18–21** the difference is 2.37 − 0.28 = 2.09 gauss. The same variation is noted for the semiquinones **12** and **21**. The introduction of the double bond at C-5–C-6 in the bicyclo[2.2.2]octane system thus causes $a_{syn}{}^{\mathrm{H}}$ and $a_{anti}{}^{\mathrm{H}}$ to both increase by a constant amount. A resonance structure of type **28** would appear to provide a mechanism. The methylene spin density would be



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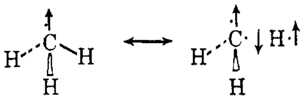
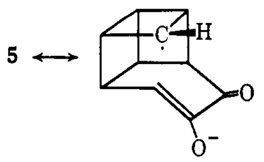
expected to be transmitted about equally to *syn-* and *anti*-hydrogen atoms. The contribution of structure **28** required to give the observed increase in a^{H} for the *syn* and *anti* hydrogens is difficult to estimate since the methylene carbon in **26** bearing the unpaired spin is tetrahedral. If planar, a contribution of **28** of 2% would predict the value of $a_{syn}{}^{\mathrm{H}} = 0.5$ gauss but the sign of a^{H} would be negative due to the spin polarization mechanism involved ($Q = -23$ gauss). The homohyperconjugation mechanism (structure **14**) predicts a

positive value of $a_{anti}{}^{\mathrm{H}}$ and a second mechanism with a negative value of a^{H} would thus result in a decrease of the hfsc for the *anti*-hydrogen atom. The magnitude of the hfs predicted for the hydrogen atom of the tetrahedral methyl radical is not −23 gauss as for the planar radical but +15 gauss (due to overlap of the free-radical orbital and the carbon–hydrogen bond).[21] If this



calculated value is reasonable, it is possible to rationalize the observed results in terms of a contribution of 3–4% for each structure **28** to the over-all resonance hybrid. This would involve a delocalization of 12–16% of the carbonyl carbon spin density by the two equivalent structures **28**.

The value of $a_{syn}{}^{\mathrm{H}}$ in **5** is considerably greater than in any of the other saturated bicyclo[2.2.2]octane semidiones. This may reflect the difference in geometry between **5** and **6–11**. However, we feel that it is probable due to the steric strain in **5**. In the case of **5** this can be rationalized in terms of contribution of structure **29**. Indeed the reason for detectable contributions of structures **28** and **29** may be a result of increased strain



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in these systems relative to structure **6**. In fact we have found this same steric driving force for carbon–carbon hyperconjugation in acyclic semidiones. Thus the value of $a_{\mathrm{CH_3}}{}^{\mathrm{H}}$ increases (from 0.05 gauss to 0.2 gauss) in the series $\mathrm{RC(O\cdot){=}C(O^-)CH_2CH_3} < \mathrm{RC(O\cdot){=}C(O^-)CH(CH_3)_2} < \mathrm{RC(O\cdot){=}C(O^-)C(CH_3)_3}$.

The previously developed argument can be approached in the opposite direction. The data suggest two mechanisms for interaction of $a_{anti}{}^{\mathrm{H}}$ and $a_{syn}{}^{\mathrm{H}}$: one stereoselective and one nonstereoselective. Furthermore the data require that the sign of splitting for both mechanisms is the same. If we assume the hyperconjugation mechanism (structure **28**) is responsible for the nonstereoselective interaction with a positive coupling constant, then the sign of the stereoselective (*anti*-H) coupling is also defined as positive, in line with the suggested homohyperconjugation mechanism. Alternatively, if one accepts the two suggested delocalization mechanisms (structures **14** and **28**) it can be argued from our data that the coupling of hydrogens attached to a tetrahedral carbon radical is positive.

The 0.09-gauss triplet splitting in **5** may represent a contribution from structure **30**. Using $Q = +14$,

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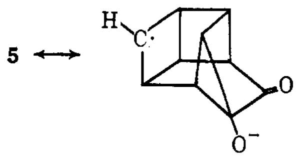
[21] R. W. Fessenden, *J. Phys. Chem.*, 71, 74 (1967).



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the contribution of the four equivalent structures **30** to the total resonance hybrid would be about 1%. Thus about 2% of the carbonyl carbon spin density may be delocalized in this manner.

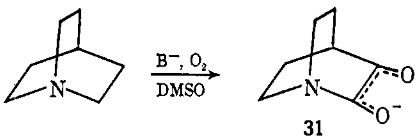
In the bicyclo[2.2.1]heptane-2,3-semidione system[7] the *anti*-hydrogen atom at C-7 has a hfsc >6 gauss. However, hyperfine splitting by *anti*-methyl at C-7 cannot be detected, although hyperfine splitting by methyl groups at C-1 and *syn*-C-7 can be detected.

The suggestions made in the previous discussion can be presumably tested experimentally by measurement of the signs of the splitting constants and by measurement of ^{13}C-hfs for ^{13}C substituted at appropriate positions in the bicyclo[2.2.2]octane system. This is a problem we are not pursuing, in part due to the fact that the α-diketones required as precursors to the semidiones in the bicyclo[2.2.2]octane system are relatively inaccessable compounds and in part due to the fact that the major hfs observed appear to be adequately explained by homohyperconjugation and by 1,3-π overlap.

The absence of hfs by bridgehead hydrogen atoms in semiquinones **12** and **21** is consistent with the conclusion of Stock and Suzuki in regard to triptycene semiquinone.[22]

An alternative interpretation of the hfsc of *syn*-hydrogen atoms in unsaturated bicyclic semiquinones, *e.g.*, **18–22**, involving more extensive delocalization has been advocated by Kosman and Stock[10] and by Nelsen and Trost.[23]

One aza derivative of bicyclo[2.2.2]octanesemidione has been examined. 3-Quinuclidinone reacts with oxygen in basic solution to form a radical anion to which structure **31** is assigned. Hyperfine splitting by the nitrogen atom was not observed.



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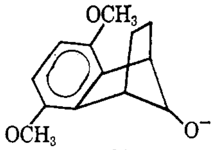
a^H (4) = 1.6 gauss
a^H (4) = 0.8 gauss

Hyperfine splitting patterns cannot differentiate between a semidione and its decarbonylated analog, a ketyl (*e.g.*, **18** and **32**).



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For **18** we have measured hyperfine splitting by ^{13}C in natural abundance and ^{17}O introduced by exchange between the diketone and labeled water. The observed values of a^C = 6.15 gauss (attributed to the carbonyl carbon)[24] in dimethoxyethane and a^O = 9.95 gauss in dimethoxyethane at 25° appear to exclude the ketyl structure in which a value of a^C approaching 50 gauss would be expected.[25]

Experimental Section

Esr Spectra. The spectra were recorded in dimethyl sulfoxide solution at approximately 25° by techniques previously described.[4,11] Spectrometer scans were calibrated in gauss by *p*-benzosemiquinone in 85% ethanol.[26] Semidiones **6**, **7**, **8**, **9**, **11**, and **13** were prepared by oxidation of the monoketone. Semidiones **5**, **15–20**, and **26** were prepared by reduction of the diketone with the enolate anion of propiophenone. Attempts to prepare semidiones **15–20** by oxidation of the monoketones were unsuccessful. In addition, 15- or 16-keto-16-noratisirane[27] failed to yield an esr signal. Semiquinones **21** or **22** were formed spontaneously from the hydroquinones in DMSO solutions of potassium *t*-butoxide.

Reagents. **Bicyclo[2.2.2]octan-2-one** was prepared by oxidation of the octanol with chromium trioxide in aqueous acetic acid solution. The ketone had mp 175–177° (lit.[28] mp 172–173°).

endo,endo-**5,6-Dimethylbicyclo[2.2.2]octan-2-one** was prepared from the *endo* adduct of maleic anhydride and 1,3-cyclohexadiene. The adduct, mp 146–147°, was formed in 89% yield from the reaction of 51 g of maleic anhydride and 42 g of 1,3-cyclohexadiene for 8 hr at 27° in 150 ml of benzene. The *endo* adduct (34.3 g) was extracted in a Soxhlet extractor into a solution of 10 g of lithium aluminum hydride in 500 ml of ether to yield 48% of *endo,endo*-**5,6-dimethylolbicyclo[2.2.2]oct-2-ene,** mp 93–94°. The dimethylol derivative was converted into the ditosylate, mp 102–104°, by reaction of 30 g of *p*-toluenesulfonyl chloride with 10 g of the alcohol in 120 ml of pyridine at −5°. After storage at 0° for 60 hr, a 69% yield of the ditosylate was isolated by addition of the pyridine solution to ice water. The ditosylate (18 g) was extracted *via* a Soxhlet extractor into a solution of 8 g of lithium aluminum hydride in 300 ml of ether. After refluxing for 20 hr, the solution was hydrolyzed and 3.14 g (57.5%) of *endo,endo*-**5,6-bicyclo[2.2.2]oct-2-ene,** bp 145–148° (749 mm), isolated by distillation. Boron trifluoride etherate (2 g) in 5 ml of diglyme was added to a mixture of 2.87 g of the octene, 0.5 g of sodium borohydride, and 15 ml of diglyme. After 1 hr the reaction was hydrolyzed by 2 ml of water, 5 ml of 3 *M* sodium hydroxide, and 5 ml of 30% hydrogen peroxide. Extraction by ether gave a 60.5% yield of *endo,endo*-**5,6-dimethylbicyclo[2.2.2]octan-2-ol,** mp 94–96°. Treatment of 1.5 g of the alcohol with 0.65 g of chromium trioxide and 0.9 ml of water in 55 ml of glacial acetic acid for 8 hr at 27° resulted in a 75% yield of *endo,endo*-**5,6-dimethylbicyclo[2.2.2]octan-2-one,** mp 67.5–68.5°, isolated by dilution of the acetic acid solution by water. The ketone had a ν_{CO} 5.81 μ (CCl_4). The nmr spectrum showed methyl peaks at −0.75 and −0.93 ppm relative to tetramethylsilane at 60 MHz. *Anal.* Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.66. Found: C, 78.78; H, 10.82.

Bicyclo[2.2.2]oct-5-en-2-ol was prepared by the reaction of vinyl acetate and 1,3-cyclohexadiene.[29] Hydrolysis of the acetate followed by oxidation of the alcohol by chromium trioxide[30] yielded **bicyclo[2.2.2]oct-5-en-2-one.** A mixture of 3 g of the ketone, 2.7 g of selenium dioxide, and 15 ml of xylene was stirred and refluxed for 4 hr. The mixture was filtered and the xylene evaporated to yield a gum from which a 9.3% yield of **bicyclo[2.2.2]-oct-5-ene-2,2-dione,** mp 78–79°, was isolated by vacuum sublimation. The ketone had ν_{CO} 5.72 μ and an nmr spectrum of peaks at −1.96 (4 H), −3.40 (2 H), and −6.48 ppm (2 H). *Anal.* Calcd for $C_8H_8O_2$: C, 76.57; H, 5.92. Found: C, 70.47; H, 5.91.

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(22) L. M. Stock and J. Suzuki, *J. Am. Chem. Soc.*, **87**, 3909 (1965); see also T. Chiu, *K'o Hsueh T'ung Pao*, 574 (1960); *Chem. Abstr.*, **56**, 13690*d* (1961).

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

(24) E. T. Strom and G. A. Russell, *J. Chem. Phys.*, **41**, 1514 (1964).

(25) N. Hirota and S. I. Weissman, *J. Am. Chem. Soc.*, **82**, 4424 (1960).

(26) B. Venkataraman, B. G. Segal, and G. K. Fraenkel, *J. Chem. Phys.*, **30**, 1006 (1959).

(27) R. A. Bell, R. E. Ireland, and R. A. Partyka, *J. Org. Chem.*, **31**, 2530 (1966); P. Crabbé, L. H. Zalkow, and N. N. Girota, *ibid.*, **30**, 1678 (1965).

(28) H. M. Walborsky and D. F. Loncrini, *J. Am. Chem. Soc.*, **76**, 5396 (1954).

(29) H. L. Goering, R. W. Greiner, and M. R. Sloan, *ibid.*, **83**, 1391 (1961).

(30) A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemin, *J. Chem. Soc.*, 2548 (1953).

Benzobicyclo[2.2.2]oct-5-en-2-one was prepared essentially by the method of Kitahonoki and Takano.[31] The ketone (1.4 g) was mixed with 0.8 g of selenium dioxide in 6 ml of xylene and the mixture refluxed for 17 hr. The solution was filtered and the xylene evaporated. The resulting residue was crystallized from pentane–benzene to give **benzobicyclo[2.2.2]oct-5-ene-2,3-dione:** mp 123–125°; ν_{CO} 5.69, 5.76 μ; mass spectrum, parent ion at *m/e* 186; nmr at −2.11 (center of complicated 4 H multiplet), −3.98 (2 H multiplet), and −7.31 ppm (4 H). *Anal.* Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.19; H, 5.49.

1,4-Dihydro-1,4-ethanonaphthalene-5,8-diol, mp 173–175°, was prepared from 1,3-cyclohexadiene and *p*-benzoquinone according to the procedure of Diels and Alder.[32] The hydroquinone was reduced to **1,2,3,4-tetrahydro-1,4-ethanonaphthalene-5,8-diol** by reduction in benzene solution using 10% palladium on carbon as the catalyst. After 10 hr the reduced diol was recovered from the benzene solution, mp 204–206° (lit.[33] mp 201–206°). Use of 1,4-dideuterio-1,3-cyclohexadiene[34] yielded **1,4-dideuterio-1,4-ethanonaphthalene-5,8-diol.** To 33 g of 1,4-dihydro-1,4-ethanonaphthalene-5,8-diol under a nitrogen atmosphere was added 44 g of sodium hydroxide in 250 ml of water. The solution was cooled to 0° and 139 g of dimethyl sulfate was added over a 25-min period. After 4 hr the brown solid that had formed was dissolved in ether. Evaporation of the ether gave an oil which was crystallized from pentane solution at −10° to yield 32 g of **5,8-dimethoxy-1,4-dihydro-1,4-ethanonaphthalene,** mp 56–57°. The nmr spectrum showed absorption at −1.46 (4 H, complex), −3.77 (6 H, sharp singlet), −4.42 (2 H, multiplet), −6.50 (2 H, multiplet), and −6.58 ppm (2 H, singlet). Use of 1,4-dideuterio-1,4-ethanonaphthalene-5,8-diol led to **5,8-dimethoxy-1,4-dideuterio-1,4-ethanonaphthalene.**

A mixture of 10.5 g of boron trifluoride etherate in 15 ml of diglyme was added over 2 hr to a mixture of 20 g of 5,8-dimethoxy-1,4-dihydro-1,4-ethanonaphthalene, 2.6 g of sodium borohydride, and 55 ml of diglyme. After 1 hr reaction the mixture was hydrolyzed by 8 ml of water and oxidized by 20 ml of 3 *M* sodium hydroxide and 20 ml of 40% hydrogen peroxide. Dilution with 600 ml of water and ether extractions yielded 21 g of **5,8-dimethoxy-1,2,3,4-tetrahydro-1,4-ethanonaphthalen-2-ol,** mp 85–87°. In a similar fashion **5,8-dimethoxy-1,4-dideuterio-2,3-dihydro-1,4-ethanonaphthalen-2-ol** was prepared.

The alcohol (0.7 g) in 10 ml of pyridine was added over a 10-min period to a mixture of 0.8 g of chromium trioxide in 15 ml of pyridine. After 15 hr at 27° the mixture was poured into 300 ml of water; **5,8-dimethoxy-1,2,3,4-tetrahydro-1,4-ethanonaphthalen-2-one** was isolated by extraction with pentane. The ketone was sublimed at 80° and 4 mm: mp 84.5–86°; ν_{CO} 5.77 μ; mp of 2,4-dinitrophenylhydrazone, 187–188°. The nmr spectrum in carbon tetrachloride gave a multiplet at −1.70 (4 H), a multiplet at −2.04 (2 H), a sharp singlet at −3.70 (6 H), a multiplet at −3.79 and −3.89 (single hydrogen atoms), and a sharp singlet at −6.57 ppm (2 H atoms). *Anal.* Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.21; H, 6.83. In a similar fashion **5,8-dimethoxy-1,4-dideuterio-2,3-dihydro-1,4-ethanonaphthalen-2-one** was prepared. The ketone (2.0 g) was refluxed for 4 hr with 1 g of selenium dioxide and 15 ml of xylene. The hot solution was rapidly filtered. The filtrate deposited yellow crystals upon cooling. Recrystallization from benzene yielded **5,8-dimethoxy-1,2,3,4-tetrahydro-1,4-ethanonaphthalene-2,3-dione,** mp 210–211°, after sublimation at 140° and 2 mm. The mass spectrum gave a parent ion at *m/e* 246 while ν_{CO} 5.71 and 5.77 μ. The nmr spectrum showed a complex multiplet at −2.06 (4 H), a sharp singlet at −3.79 (6 H), a multiplet at −4.41 (2 H), and a sharp singlet at −6.81 ppm (2 H atoms). *Anal.* Calcd for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 68.10; H, 5.89. In a similar manner **5,8-dimethoxy-1,4-dideuterio-2,3-dihydro-1,4-ethanonaphthalene-2,3-dione** was prepared. The deuterated diketone had mp 211–212° and gave a parent ion at *m/e* 248. The isotopic purity was calculated to be 98.48%. The diketone showed ν_{CO} at 5.70 and 5.78 μ (chloroform) and gave an nmr spectrum (deuteriochloroform) showing a complex multiplet at −2.05 (4 H), a sharp singlet at −3.79 (6 H) and −6.80 ppm (2 H).

5,8-Dimethoxy-1,2,3,4-tetrahydro-1,4-ethanonaphthalen-2-one (600 mg) was dissolved in a mixture of 99% *o*-deuterioacetic acid, 2 ml of 99.5% deuterium oxide, and 6 drops of concentrated sulfuric acid. The solution was heated at 90° for 10 days. The ketone was isolated by addition of water and treated with slightly basic ethanol at 27° for 2 hr. The isolated **6,7-dideuterio-5,8-dimethoxy-1,2,3,4-tetrahydro-1,4-ethanonaphthalen-2-one** had mp 84–86°. The nmr spectrum was similar to the nondeuterated compound except that the sharp singlet at −6.57 ppm could hardly be detected.

Selenium dioxide oxidation yielded **6,7-dideuterio-5,8-dimethoxy-1,2,3,4-tetrahydro-1,4-ethanonaphthalene-2,3-dione,** mp 211–212°, after sublimation at 140°. The mass spectrum gave a parent ion at *m/e* 248 and a calculated isotopic purity of 90.6%. The nmr spectrum showed a very small peak at −6.80 ppm.

Dibenzobicyclo[2.2.2]octa-2,5-diene-7,8-dione was prepared from the adduct of maleic anhydride and anthracene.[35] The diacid was decarboxylated with lead tetraacetate by the method of Kitahonoki and Takano[31] to yield **dibenzobicyclo[2.2.2]octa-2,5,7-triene** which was hydroborated to yield **dibenzobicyclo[2.2.2]octa-2,5-dien-7-ol,** mp 141–142° (lit.[36] mp 142–143°). **Dibenzobicyclo[2.2.2]octa-2,5-dien-7-one** was prepared by the procedure of Wawzonek and Hallum.[36] The ketone was oxidized with selenium dioxide[37] to yield dibenzobicyclo[2.2.2]octa-2,5-diene-7,8-dione, mp 199.5–201° (lit.[37] mp 199–201.5°).

Acknowledgment. The following substances were obtained as gifts: pentabicyclo[$4.2.0^{2,5}.0^{3,8}.0^{4,7}$]decane-9,10-dione from S. Masamune;[38] bicyclo[2.2.2]octane-2,3-dione from P. Yates; bicyclo[2.2.2]octanyl acid phthalate from H. M. Walborsky;[28] 1-methoxy-4-methylbicyclo[2.2.2]octan-2-one, 1-methyl-4-(N-piperidinyl)bicyclo[2.2.2]octan-2-one, and 4,6-dimethyl-1-methoxybicyclo[2.2.2]octan-2-one from K. Morita;[15] the precursors to **10** (8-keto and 7-keto-8-hydroxy) from O. E. Edwards;[39] the precursor to **11** from L. H Zalkow (compound IV, ref 2b); 16-noratisiranone-15 and -16 from L. H. Zalkow[27] and R. Ireland;[27] and the precursor to **26** from J. W. Gates, Jr., of Eastman Kodak Co.[40] The spectrum of the semidione obtained from 3-quinuclidinone was recorded by Mr. John McDonnell. The ^{13}C and ^{17}O hyperfine splittings in **18** were measured by Dr. Graham Underwood. Bicyclo[2.2.2]oct-5-en-2-one was prepared by Dr. L. G. Schnack.

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[31] K. Kitahonoki and Y. Takano, *Tetrahedron Letters*, 1597 (1963).

[32] O. Diels and K. Alder, *Ber.*, **62**, 2337 (1929).

[33] R. B. Thompson, U. S. Patent 2,903,368 (1959).

[34] B. Franzus, *J. Org. Chem.*, **28**, 2954 (1963).

[35] O. Diels and K. Alder, *Ann.*, **486**, 191 (1931).

[36] S. Wawzonek and J. V. Hallum, *J. Org. Chem.*, **18**, 288 (1953).

[37] W. R. Vaughan and M. Yoshimine, *ibid.*, **22**, 528 (1957).

[38] S. Masamume, H. Cots, and M. G. Hogben, *Tetrahedron Letters*, 1017 (1966).

[39] D. Dvornik and O. E. Edwards, *Can. J. Chem.*, **35**, 860 (1957).

[40] D. D. Chapman, H. S. Wilgus, III, and J. W. Gates, Jr., *Tetrahedron Letters*, 6175 (1966).