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# Aliphatic Semidiones. XXV. Bicyclo[*n*. 2.1]alkane-2,3-semidiones[1]

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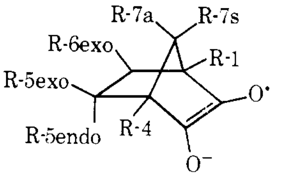
**Abstract:** The esr spectra of a number of bicyclo[2.2.1]heptane-2,3-semidiones and bicyclo[3.2.1]octane-2,3-semidiones are reported, including tri- and tetracyclic derivatives. Assignments of hyperfine splitting constants have been made by studies of deuterium and alkyl derivatives. A number of long range transoid, coplanar interactions between protons and the electron spin are reported, discussed, and analyzed in terms of valence bond resonance structures. Extended Hückel and/or INDO calculations are reported for bicyclo[2.2.1]heptane-2,3-semidione and several alkyl derivatives, the corresponding semifuraquinone, bicyclo[2.2.1]hept-5-ene-2,3-semidione, and the semifuraquinone derivative and *exo*- and *endo*-tricyclo[3.2.1.$0^{2,4}$]octane-6,7-semidiones.

Esr hyperfine splittings (hfs) by hydrogen atoms separated from a center of spin density by three or four bonds have been reported for a few monocyclic species such as cyclobutyl, cyclopentyl, and cyclohexyl radicals,[4] piperidine nitroxide,[5,6] and cycloheptanesemidione.[7] Resolution of these long range hfs requires a frozen conformation for the monocyclic system. Rigid bicyclic structures are often rich in such long range hfs.[8,9] Since our original report of such long range hfs in bicyclic 1,2-semidiones,[8,9] similar observations have been reported for other spin centers including alkyl radicals,[10-12] nitroxides,[13,14] semiquinones,[15,16] semifuraquinones,[17] dicyanoethylene radical anions,[18] dimethyldialkylhydrazine radical cations,[19] and 1,4-semidiones.[16,20]

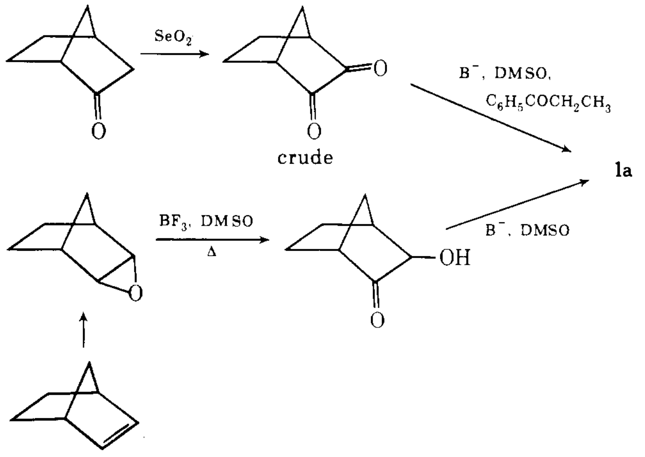
The present results complement previous reports on long range splittings in 2,3-semidiones derived from bicyclo[*n*.1.0]alkanes,[21] bicyclo[*n*.1.1]alkanes,[22] bicyclo[2.2.2]alkanes,[23,24] bicyclo[3.2.0]octanes,[7,9,23] bicyclo[3.2.2]nonanes,[9,25] bicyclo[3.3.1]nonanes,[9] bicyclo[3.3.2]decanes,[25] and a variety of polycyclic derivatives of cyclobutanesemidione.[26]

**Synthesis of Bicyclo[2.2.1]heptanesemidiones.** Treatment of bicyclo[2.2.1]heptan-2-one with traces of oxygen in basic DMSO solution failed to yield the esr signal of the semidione although this technique can be applied to a wide variety of cyclohexanone derivatives.[27,28] Reaction of this ketone, and most other bicyclo[2.2.1]heptan-2-ones not containing a *syn*-7 substituent with selenium dioxide, failed to yield significant amounts of the $\alpha$-diketone although the crude product from norcamphor did yield the esr signal of **1a** when treated with the propiophenone enolate ion in DMSO.[8]



**1a**, unsubstituted
(R unspecified = H)
**b**, R-7a = D
**c**, R-7s = D
**d**, R-5,6exo = D
**e**, R-7 = $CH_3O$
**f**, R-1,4 = D; R-7 = $CH_3O$
**g**, R-1 = $CH_3$
**h**, R-7a = $CH_3$
**i**, R-7a = $CD_3$
**j**, R-7s = $CH_3$
**k**, R-1,7s = $CH_3$
**l**, R-7 = $CH_3$
**m**, R-1,7,7 = $CH_3$
**n**, R-1,7s = $CH_3$; R-7a = $CD_3$
**p**, R-5,6exo = $CH_3$
**q**, R-5,6endo = $CH_3$

**Scheme I**



An *in situ* preparation of 3-hydroxy-2-norbornanone from norbornene oxide in DMSO containing a trace of boron trifluoride etherate (80°, 24 hr)[29] yielded **1a** when the DMSO solution was treated with potassium *tert*-butoxide (Scheme I), but this method gave mixtures of radicals when applied to other substituted norbornenes. 3-Bromonorcamphor in basic DMSO also yielded **1a** but this method[30] failed for 3-bromocamphor itself.

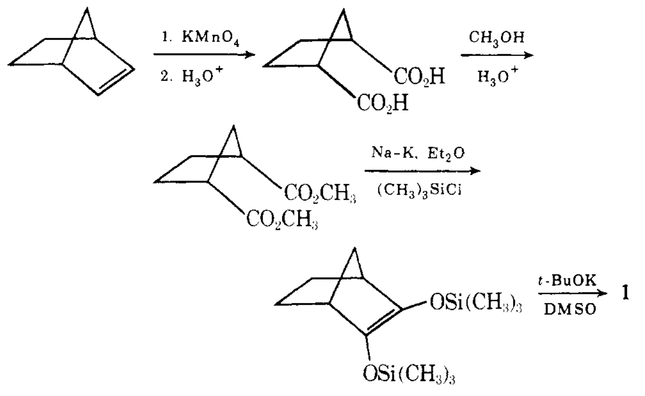
**Table I.** Hyperfine Splitting Constants of Bicyclo[2.2.1]heptane-2,3-semidione in DMSO at 25°, $K^+$ Gegenion

| Semidione | Substituents | $a^H$ (G) C-1,4 | C-5,6endo | C-5,6exo | C-7s | C-7a | $CH_3$ |
|---|---|---|---|---|---|---|---|
| **1a**[a] | None | 2.49 | <0.1 | 2.49 | 0.36 | 6.48 | |
| **1b**[a] | *anti*-7D | 2.50 | <0.1 | 2.50 | 0.40 | 1.0[b] | |
| **1c**[a] | *syn*-7D | 2.50 | <0.1 | 2.50 | | 6.50 | |
| **1d**[a] | *exo,exo*-5,6-$D_2$ | 2.50 | <0.1 | 0.40[b] | 0.40 | 6.48 | |
| **1e**[c] | 7,7-dimethoxy | 1.96 | <0.1 | 2.50 | | | |
| **1f**[c] | 1,4-$D_2$-7,7-dimethoxy | 0.3[b] | <0.1 | 2.51 | | | |
| **1g**[d] | 1-methyl | 2.51 (1) | <0.1 | 2.51 | 0.46 | 6.29 | 0.14 |
| **1h**[a] | *anti*-7-methyl | 2.37 | 0.09 | 2.37 | 0.49 | | 0.19 |
| **1i**[a] | *anti*-7-$CD_3$ | 2.38 | <0.1 | 2.38 | 0.50 | | |
| **1j**[d] | *syn*-7-methyl | 2.52 | <0.1 | 2.52 | | 3.11 | 0.18 |
| **1k**[d] | 1,*syn*-7-dimethyl | 2.55 (1) | <0.1 | 2.55 | | 3.05 | 0.18, 0.18 |
| **1l**[c] | 7,7-dimethyl | 2.07 | 0.26 | 2.90 | | | 0.53 (1) |
| **1m**[d] | 1,7,7-trimethyl | 2.08 (1) | 0.22 (1) | 3.01 | | | 0.55, 0.18 |
| **1n**[c] | 1,*syn*-7-dimethyl-*anti*-7-$CD_3$ | 2.08 (1) | 0.22 (1) | 3.01 | | | 0.55, 0.15 |
| **1p**[a] | *exo,exo*-5,6-dimethyl | 2.59 | <0.1 | | 0.40 | 6.19 | 0.18 |
| **1q**[a] | *endo,endo*-5,6-dimethyl | 2.33 | | 1.84 | 0.40 | 6.97 | 0.20 |

[a] Precursor **2**. [b] $a^D$. [c] Precursor ketone. [d] Precursor $\alpha$-diketone.

Semidiones **1a–d, h, i,** and **p** were conveniently prepared from the corresponding bis(trimethylsiloxy)norbornenes (Scheme II) which were easily prepared in three steps from the appropriate norbornene.

Scheme II



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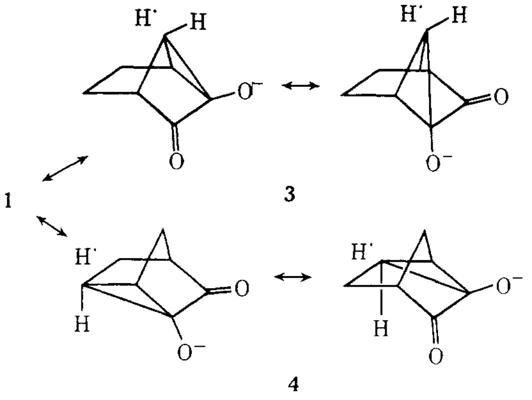
In contrast to norcamphor, 7,7-dimethoxynorbornanone and its 1,4-dideuterio derivative were easily oxidized to the semidiones **1e** and **f.** Other bicyclo[2.2.1]heptan-2-ones with a *syn*-7 substituent which yielded the semidione in basic DMSO solution or the $\alpha$-diketone with selenium dioxide were the *syn*-7-methyl, 1,*syn*-7-dimethyl, 7,7-dimethyl, and 1,7,7-trimethyl derivatives. Poor yields of the $\alpha$-diketones (*via* selenium dioxide) but no semidione in base catalyzed oxidation were detected from 1-methylnorbornan-2-one and *endo,endo*-5,6-dimethylnorbornan-2-one whereas neither the dione nor the semidione could be detected form *anti*-7-methylnorbornan-2-one or *exo,exo*-5,6-dimethylnorbornan-2-one. Apparently a *syn*-7 substituent shields the $\alpha$-diketone function from nucleophilic attack under the drastic conditions required for the oxidations.

**Assignment of Hfsc to Bicyclo[2.2.1]heptane-2,3-semidione.** Compounds **1a–f** define the values of the hfsc at C-1,4,7 and the exo positions at C-5,6 (Table I). The hfsc's at the endo position of C-5,6 were not usually detected and were therefore <0.1 G. An extremely strong long range coupling at H-7a is noted (~6.5 G) which is drastically reduced by *syn*-7-methyl substitution to ~3 G. The fairly strong W-plan coupling to H-5,6exo (~2.5 G) is also reduced by substitution of methyl groups at the C-5,6endo positions (to 1.8 G). *anti*-7-Methyl or 7,7-dimethyl substitution apparently changes the geometry of the molecule so that the hfs by H-5,6endo are observed (~0.25 G in **1l–n**) and this long range interaction is also retarded by alkyl substitution at C-1,4 (*e.g.*, **1m**). Long range interactions of methyl groups at C-1,4, C-5,6endo, C-5,6exo, C-7s, and C-7a are observed to be all of approximately equal magnitude (~0.2 G) except when 7,7-dimethyl substitutes are present whence $a_{CH_3}{}^H$ for the *syn*-7 methyl is large (~0.5 G) and for the *anti*-7-methyl is small (<0.1 G). The methyl substituents are freely rotating which reduces the magnitude of the long range interaction by *ca.* two ($\langle\cos^2\theta\rangle$) from the value expected for a hydrogen atom held rigidly in the most favorable conformation.

**Mechanisms of Long Range Interactions in Bicyclo[2.2.1]heptane-2,3-semidiones.** Extended Hückel[31a] and INDO[31b] calculations have already been reported for **1a** and **1j** which reproduced the observed hfsc (see Figure 1 and Table II). We now report EH-SCF calculations (Table II) performed by a previously described method,[21b] using the geometry of Figure 1.

All the calculations indicate $a_{7a}{}^H$ and $a_{5,6exo}{}^H$ to be positive in agreement with homohyperconjugation structures[32] **3** and **4**.

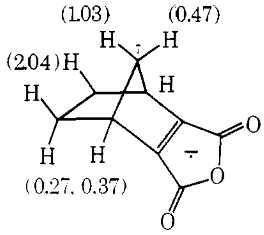


The mechanism of interaction with H-7s is not so obvious. In one approach to this problem we have performed INDO calculations for **5**[17] where the methylene group lies in a nodel plane of the spin label and delocalization to H-7 is therefore impossible.[26a] Because of the symmetry of **5** the hfsc at the methylene bridge (which lies in a nodal plane) must be determined by a spin polarization mechanism. The INDO calculation (Table II) for **5** indicates that $a^H$ for both H-7a and H-7s is negative, reasonable but not required signs for a spin polarization mechanism. We have previously pointed out that the experimental relative magnitudes of the hfsc in a geometric situation similar to the methylene group in **5** is anti/syn ~2:1,[20] consistent with hyperconjuga-

**Table II.** Molecular Orbital Calculations of $a^H$ in **1**

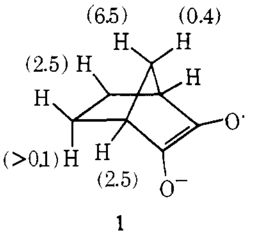
| Substituents | Method | Geometry $D$ (Å) | Geometry $\theta$, deg | Geometry $\Phi$, deg | $a^H$ (G) H-1,4 | $a^H$ (G) H-5,6exo | $a^H$ (G) H-5,6endo | $a^H$ (G) H-7s | $a^H$ (G) H-7a |
|---|---|---|---|---|---|---|---|---|---|
| None | EH[31a] | 2.286 | 134 | 115 | 1.4 | 1.5 | 0.5 | 0.3 | 6.4 |
| None | INDO[31b] | 2.286 | 125 | 110 | 1.8 | 1.8 | −0.2 | −0.8 | 5.9 |
| None | EH–SCF | 2.25 | 125 | 110 | 1.4 | 2.7 | 0.6 | 0.2 | 5.3 |
| None | EH–SCF | 2.25 | 123 | 114 | 1.9 | 1.7 | 0.2 | 0.6 | 7.3 |
| **7a**-$CH_3$ | EH–SCF | 2.25 | 123 | 114 | 1.9 | 1.7 | 0.2 | 0.5 | 0.2[a] |
| **7s**-$CH_3$ | EH[31a] | 2.286 | 134 | 115 | 1.1 | 1.6 | 0.5 | 0.1[a] | 3.2 |
| **7s**-$CH_3$ | INDO[31b] | 2.286 | 125 | 110 | 1.8 | 1.7 | −0.15 | 0.3[a] | 4.4 |
| **7s**-$CH_3$ | EH–SCF | 2.25 | 123 | 114 | 1.5 | 1.6 | 0.3 | 0.4[a] | 1.7 |
| **5** | INDO | 2.18 | 122 | 115 | −0.26 | 1.8 | 0.22 | −0.47 | −1.97 |

[a] $a_{CH_3}{}^H$, average value taken from one conformation, see Figure 1.



**5**

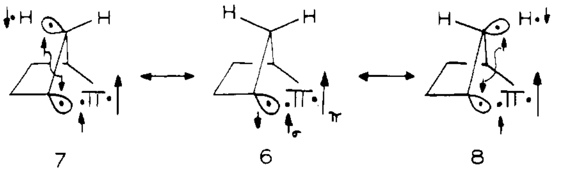
exptl $a^H$ in G[17]



**1**

exptl $a^H$ in G

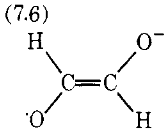
tion in the spin polarized structure **6** where **7** is twice as important as **8**.[31] We may expect the same interactions in the



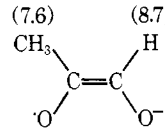
7 6 8

semidiones, and in fact the INDO calculation for **1** indicates $a_{7s}{}^H$ to be negative.[31b] If we take the value of $a_{7s}{}^H$ experimental to be −0.4 G, it follows from the above argument that the spin polarization contribution to $a_{7a}{}^H$ should be $\sim|2\ (0.4)|$ G. Depending on the sign of this contribution the magnitude of the homohyperconjugation interaction (**3**) is ~5.5 or 7.5 G (exptl 6.5 G).

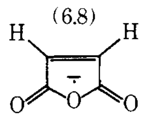
The calculated and experimental hfsc for **1** and **5** indicates that the semidione and semifuraquinone spin labels must have very nearly equal spin densities at the substituted positions. This is further demonstrated by the observed hfsc for **9–11** ($a^H$ in gauss).



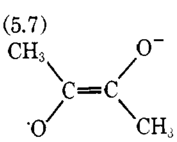
**9**[33]



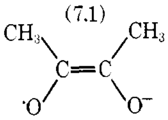
**10**[33]



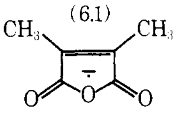
**11**[34]



**9Me**[35]



**10Me**[35]



**11Me**[17]

Another instance where the symmetry of the spin label has a large effect on the hfs is at the bridgehead positions in **1** ($a^H$ = 2.5 G) and **5** ($a^H$ = 0.4 G). In **1** the 1,2- and 1,3-interactions between the bridgehead hydrogen atoms and spin density at the carbonyl carbon atoms (*i.e.*, hyperconjugation and homohyperconjugation, respectively) reinforce each other, **12** ($a_H = a_{1,2} + a_{1,3}$), whereas in **5** the 1,2- and 1,3-interactions would be of opposite sign (**13**) and partial cancellation occurs ($a_H = a_{1,2} - a_{1,3}$). Since spin densities and geometries of **1** and **5** are similar, the equations can be solved for $a_{1,2}$ = 1.5 and $a_{1,3}$ = 1.0 G in these semidione systems.[36]

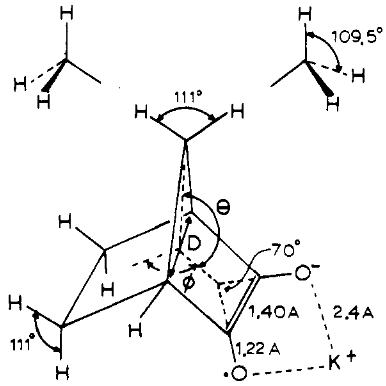
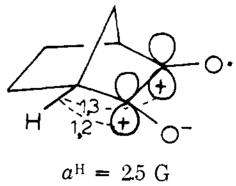
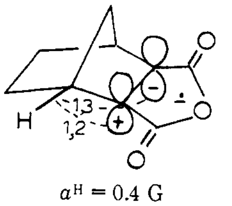


**Figure 1.** Geometries used in the molecular orbital calculations: $d$(C–C) = 1.54, $d$(C–H) = 1.09 Å. Methylene and methine hydrogens were positioned so that all H–C–C angles for a given group were equal. Substitution of a methyl group for C-7 hydrogen atoms was assumed to have no effect on geometry.

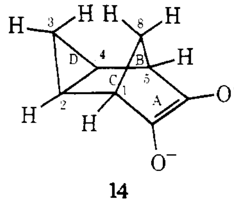


**12**

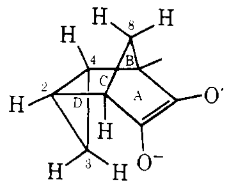


**13**

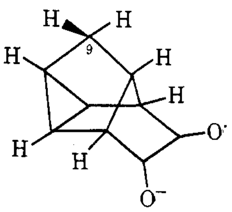
Spin delocalization was investigated in systems **14–18** by experimental assignment of hfsc and by EH-SCF calculations. Table III presents a consistent set of experimental hfsc.



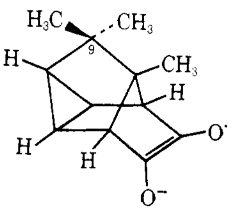
**14**



**15**



**16**

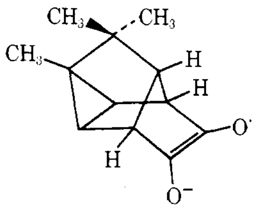


**17**

**Table III.** Experimental and Calculated Hfsc in Tricyclo[3.2.1.0$^{2,4}$]octane-6,7-semidiones **14–18**, DMSO, 25°, K$^+$ Gegenion

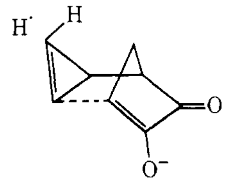
| Structure | H-1,5 | H-2,4 | H-3s | H-3a | H-8s | H-8a | H-9 |
|---|---|---|---|---|---|---|---|
| | $a^H$ (G) | | | | | | |
| **18**, exptl | 1.29 | 0.46 | | 0.09[a] | | | |
| **17**, exptl | 1.20 | 0.50 | | 3.74 | 0.07[a] | | |
| **16**, exptl | 1.33 | 0.48 | | 4.81 | *b* | | 0.21 |
| **14**, exptl | 0.98 | 0.40 | 0.20 | 3.45 | 7.61 | 1.05 | |
| **14**, calcd[c] | 0.62 | 0.01 | 0.15 | 3.09 | 5.18 | 0.33 | |
| **14**, calcd[d] | 1.04 | 0.03 | 0.35 | 2.97 | 7.54 | 0.85 | |
| **15**, exptl | 2.88 | 0.34 | 0.15 | or 0.47 | 7.78 | 1.37 | |
| **15**, calcd[c] | 2.16 | 0.66 | 1.24 | 1.55 | 6.08 | 0.73 | |
| **15**, calcd[d] | 2.25 | 0.48 | 0.56 | 0.74 | 8.06 | 1.06 | |

[a] $a_{CH_3}^H$. [b] Not detected. [c] $d$(C-1–C-5) = 2.25 Å, ∠CD = 117°, ∠AC = 110°, ∠AB = 125°. [d] $d$(C-1–C-5) = 2.25 Å, ∠CD = 117°, ∠AC = 114°, ∠AB = 123°. Other bond lengths equal to those employed in Figure 1.

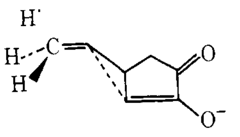


**18**

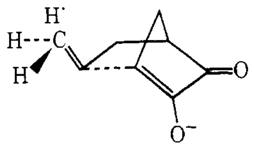
The surprising high value of $a_{3a}^H$ in **14, 16,** and **17** is well duplicated by the calculations and indicates the tendency for spin transmittal over a coplanar system of transoid bonds and orbitals, *e.g.*, resonance structure **19.** Similar structures have been previously invoked to explain the 2.5 V long range splitting in bicyclo[3.1.0]hexanes (**20**)[21] and may be involved in the hfs by exo methyl groups at C-5,6 in **1p** (**21**). Hydrogen atoms at "C-9" in **16** have a fairly strong interaction and again a 2.5 V approximately coplanar transoid arrangement of bonds and orbital is possible (**22**) as is also the case for the *anti*-7 methyl group in **1h,l,m** (**23**). This 2.5 V long range splitting which is pictured as functioning through the bonds (*e.g.*, structures **19–23**) is not reduced in magnitude by alkyl substitution at the syn positions if the geometry is not altered. This is obvious by comparison of the 2.5 V splittings at C-3 in **14** with **16** or **17** or the anti methyl group in **24** and **25.**[21] On the other hand, 2V or W-plan[37] interactions involving a through space interaction (*e.g.*, structures **3** and **4**) is impeded by syn alkyl substitution. This is obvious in comparing the hfsc for the *anti*-6-hydrogens and in **26** and **27,**[21] the *anti*-7-hydrogen in **1a** ($a^H$ = 6.5 G) and **1j** ($a^H$ = 3.1 G), or the *exo*-5,6-hydrogens in **1a** ($a^H$ = 2.5 G) and **1q** ($a^H$ = 1.84 G) or **15** ($a^H$ = 0.34 G). Other examples of this effect in 2 V long range interactions have been reported in the bicyclo[2.2.2]octane-2,3-semidiones[23,24] and in the bicyclo[3.2.1]octane-6,7-semidione.[23] The effect is predicted by INDO[31b] or EH-SCF calculations and perhaps can be interpreted as a difference in the repulsive energy between an electron pair in C–H and C–C single bonds toward the unpaired electron in the spin label.



**19**



**20**



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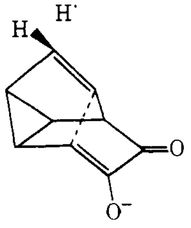

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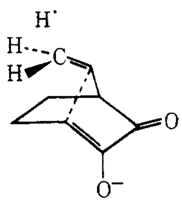

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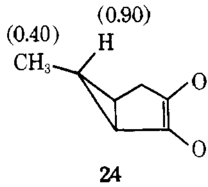

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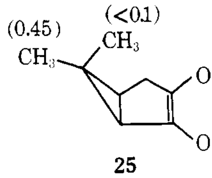
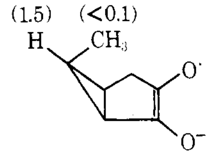
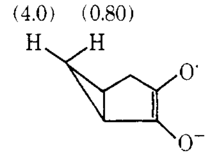


**25**



**26**

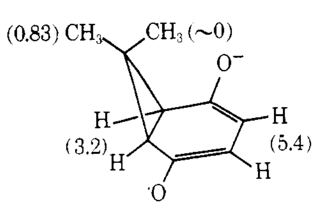


**27**

The interaction of the bridgehead hydrogens (H-1,4) in **1, 14, 15,** etc., presumably is the result of hyperconjugation in partial violation of Bredt's rule. However, structures with a double bond at the bridgehead contribute only to the extent of ~2.5 G/750 G ≃ 0.3% to the total resonance hybrid. The magnitude of $a^H$ for the bridgehead position decreases from 2.5 G in **1** to 1.0 G in **14** but increases to 2.9 G in **15.** These changes are predicted by the EH-SCF calculations (Table III) and seem to reflect the position of the HOMO nodal surface. In **14** the cyclopropyl substituent causes this nodal surface to approach closely to the bridgehead hydrogen atom while in **15** the cyclopropyl substituent pulls the nodal surface away from the bridgehead hydrogen. Another interesting fact in the calculations for **14** and **15** is that the calculated cyclopropyl methylene hfs in the exo compound (**14**) are less sensitive to structural change than the corresponding hydrogen atoms in the endo compound (Table III). This may be explained by the fact that in the endo compound the methylene group is quite close to the π-system in which the unpaired electron resides. A small change in geometry will therefore cause a larger change in the atomic orbital overlap between these parts of the system and would cause a larger change in the predicted hfsc for the endo methylene bridge (**15**) than for the exo bridge

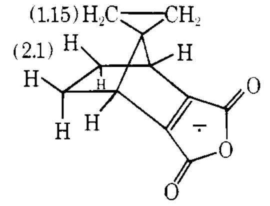
(**14**). This same proximity effect is apparently responsible for the hfs of methyl groups at *syn*-C-7 and *endo*-C-5,6 in **1**.[38]

The relative magnitudes of $a_{\mathrm{CH_3}}{}^{\mathrm{H}}$ in the bicyclo[2.2.1] system are *syn*-7-methyl > *anti*-7-methyl (*e.g.*, **11,m**). However, in the bicyclo[3.1.0] system the reverse is true, *anti*-6-methyl (**24**) > *syn*-6-methyl (**25** or **26**).[21] The EH-SCF calculations faithfully reproduce this effect by predicing $a_{syn\text{-}\mathrm{CH_3}}{}^{\mathrm{H}}/a_{anti\text{-}\mathrm{CH_3}}{}^{\mathrm{H}} = 2$ for the bicyclo[2.2.1]heptane system (Table II) and 0.25 for the bicyclo[3.1.0]hexane system (Figure 1 of ref 21b). These observations are probably the result of geometry which positions the syn methyl group in the bicyclo[2.2.1] system for better through space interaction whereas the anti methyl group in the bicyclo]3.1.0] system can form a better coplanar, transoid arrangement of bonds and orbitals (*i.e.*, **21**). Another aspect of this 2.5 V interaction is that spin polarization and delocalization effects can be of opposite sign and cancellation can occur. This seems to be particularly true for *anti*-7-alkyl groups in the bicyclo[2.2.1]heptane-2,3-semidione. When the symmetry of the spin label is chosen so that spin delocalization is impossible (**28–30**), it is observed that the anti spin-polarization interaction is actually more important than the effect in the syn positions. The explanation of the stereoelectivity of the interactions of **28–30** appears to be that after the spin has been polarized in the $\sigma$-bond attached to the spin label (*e.g.*, **6**) a further transmission by a W-plan interaction is highly stereoselective as it is in **1** itself.



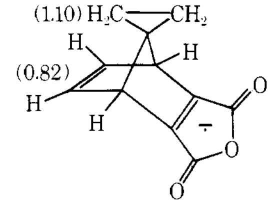
**28**[20]

$a^{\mathrm{H}}$ in G



**29**

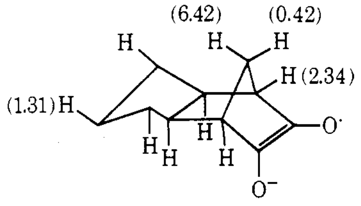
unassigned, $a^{\mathrm{H}}$ = 0.46(2), 0.23(4) G (see also ref. 17b)



**30**[17]

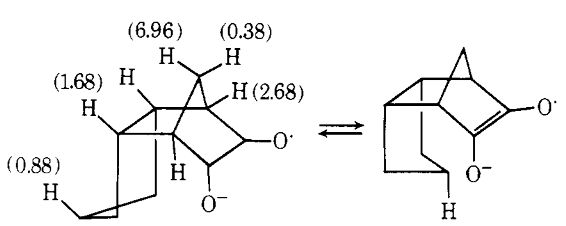
unassigned, $a^{\mathrm{H}}$ = 0.46(2), 0.55(2) G

Semidiones **31** and **32** were synthesized from the corresponding bis(trimethylsiloxy)alkenes which were not isolated in pure form.[26] In **31** there is evidence for a 3V long range hfs of 1.31 G. Previously reported 3V interactions in bicyclic semidiones have been 0.7 and 1.06 G (structures **19** and **23** in ref 26b) and 0.09 G for the methyl group in **18**. In semidiones where two systems of bonds connect the spin label with the hydrogen atom in a coplanar transoid manner, the fall-off from a 2 V (~6–10 G) to a 2.5 V (~3–5 G) to a 3 V (0.7–1.5 G) is about a factor of 2.5 for each additional bond. The magnitude of the interaction is about the same as would be expected for a full unit of spin connected to a hydrogen atom by only one system of bonds since for a symmetrical semidione a hydrogen atom in the nodal plane will have a hfsc proportional to $(c_1 + c_2)^2$ where $c_1$ and $c_2$ are the MO coefficients at the carbonyl carbon atoms in the HOMO. Since $c_1 = c_2 \simeq 0.5$ in the semidiones,[35b] it follows that $(c_1 + c_2)^2 \sim 1.0$ and is equivalent to a full unit of spin localized at one carbon atom.



**31**

unassigned, $a^{\mathrm{H}}$ = 0.10(2) G

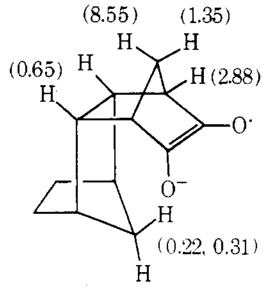


**32a**

**32b**

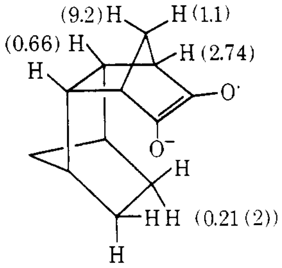
unassigned, $a^{\mathrm{H}}$ = 0.17(2) G

Semidione **32** gives evidence for a considerable interaction with one of the methylene hydrogen atoms in the trimethylene substituent. Perhaps structure **32b** is present and a through space proximity interaction occurs. Two tetracyclic derivatives of **32** have been investigated. Semidiones **33** and **34** were prepared from the diesters by the bis(trimethylsiloxy)alkene route. They are considerably more stable than **1** or **32** and show no sign of decomposition over a 30 hr period in DMSO solution. The hfsc have been assigned by analogy to **1** and its other derivatives. Both $a_{7a}{}^{\mathrm{H}}$ and $a_{7s}{}^{\mathrm{H}}$ seem to be enhanced in **33** or **34** over **32** or **1**. The endo substituents at C-5,6 reduce the magnitude of $a_{5,6exo}{}^{\mathrm{H}}$ considerably (from 2.5 G in **1** to 1.68 G in **32** to 0.65 G in **33** or **34**).



**33**

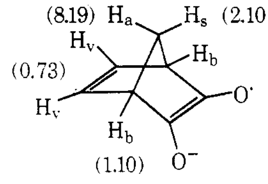
$a^{\mathrm{H}}$ in G



**34**

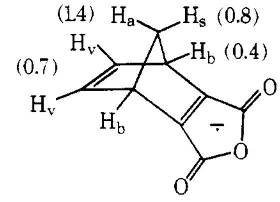
$a^{\mathrm{H}}$ in G

**Bicyclo[2.2.1]hept-5-ene-2,3-semidiones.** Bicyclo[2.2.1]hept-5-ene-2,3-semidione (**35**) is considerably less stable than **1**. Oxidation of the monoketone in basic solution fails to yield **35**. Treatment of the $\alpha$-hydroxy ketone or diketone[39] with base in DMSO also fails to produce the semidione. The semidione has been observed by electrolysis of the dione in DMSO or by reaction of *endo*-3-*tert*-butyldimethylsiloxybicyclo[2.2.1]hept-5-en-2-one[40] with base and DMSO in a flow system (Figure 2).



**35**

$a^{\mathrm{H}}$ in G



**36**[17]

$a^{\mathrm{H}}$ in G

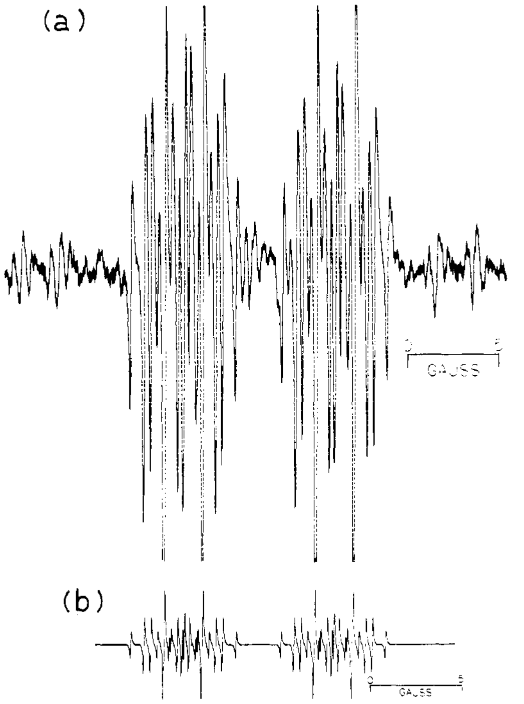
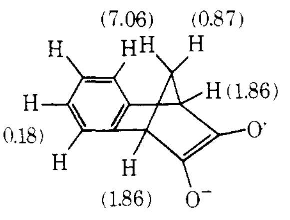


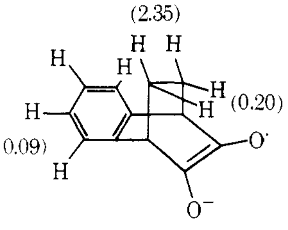
**Figure 2.** First derivative esr spectrum of **35**: (a) radical anion obtained by treatment of *endo*-3-*tert*-butyldimethylsiloxybicyclo[2.2.1]hept-5-en-2-one with base in DMSO, (b) spectrum calculated with hfsc in text. In the wings of spectrum a, peaks due to bicyclo[3.2.0]hept-2-ene-6,7-semidione can be seen.

Reduction of benzobicyclo[2.2.1]hepten-2,3-dione[41] by propiophenone enolate anion in DMSO gave the radical anion (**37**) which could be detected for ~10 min after generation. The hfs of the aromatic protons are in reasonable agreement with those previously reported for **38**[24] and support a delocalization (homoallylic) between the two π-systems which have similar symmetries in their HOMO. The observation of $a_{\text{Ar}}^{\text{H}} = 0.18$ in **37** is consistent with a total aromatic carbon spin density of 6(0.18/24)100 = 4.5% of an electron spin. In **38** the aromatic spin density is only 2.25% but in the dibenzo derivative of bicyclo[2.2.2]octadiene-2,3-semidione the total spin density in the two aromatic rings is 7.5% of the unpaired electron spin.[24]



**37**

$a^{\text{H}}$ in G



**38**

$a^{\text{H}}$ in G

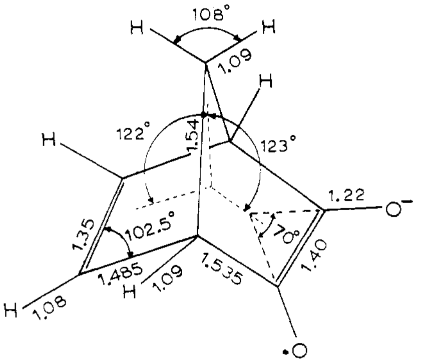
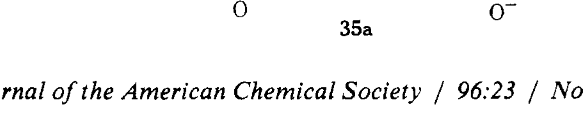


**Figure 3.** Geometries (distance in angströms) employed in INDO calculation of **35** and **36**. Methine and vinyl hydrogens were adjusted so that all H-C-C angles for a given hydrogen were equal. For the semifuraquinone spin label a planar geometry with *d*(C=C) = 1.4 Å, *d*(C=O) = 1.22 Å, *d*(C—O) = 1.36 Å, ∠CCC = 107.89°, ∠CCO = 105.92°, and ∠COC = 112.38° was employed.

**Table IV.** Calculated and Experimental Hfsc for **35–36**

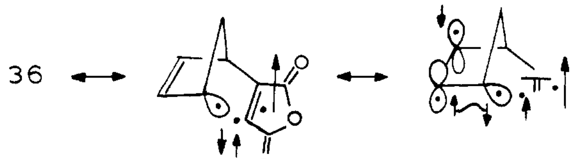
| | $a^{\text{H}}$ in G | | | |
|---|---|---|---|---|
| Structure | $H_v$ | $H_b$ | $H_a$ | $H_s$ |
| **35**, calcd | −0.52 | +0.96 | +3.46 | −0.16 |
| **35**, exptl | 0.73 | 1.10 | 8.19 | 2.10 |
| **36**, calcd | +1.56 | +0.14 | −1.82 | −0.77 |
| **36**, exptl[17] | 0.8 | 0.4 | 1.4 | 0.8 |



**35**

**35a**

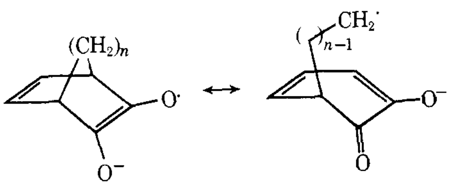
The question of spin delocalization in **35** has been investigated by INDO calculations for **35** and **36**. Table IV lists the calculated values of $a^{\text{H}}$ for **35** using the geometry of Figure 3. The calculation for **35** is in agreement with the concept that a positive spin density on $C_{\text{vinyl}}$ arises in **35** by a 1,3 π overlap, *e.g.*, **35a**. Spin polarization of the vinyl carbon-hydrogen bond ($Q \sim -23$) would then give rise to a negative value of $a_{\text{vinyl}}^{\text{H}}$. However, when the calculation for **36** is considered it is obvious that another effect cannot be ignored. In **36** orbital symmetries would prohibit the π-π overlap between the HOMO's of the olefin and the spin label. It appears, however, that spin polarization of the C-1-C-2 bond provides a way of introducing negative spin density to the vinyl carbon atoms by allylic-type resonance, *e.g.*, **37** and **38.** This spin polarization mechanism should be of about equal importance for π = semifuraquinone and semidione because of the nearly equal spin densities involved. We thus conclude that the value of $a_{\text{vinyl}}^{\text{H}}$ = (calculated) −0.5 for **35** is the net effect of nearly equivalent π delocalization (*ca.* −2.0 G) and spin polarization (*ca.* +1.5 G) effects. In view of the possible fortuitous cancellation and possible changes in sign of $a_{\text{vinyl}}^{\text{H}}$, it is obvious that considerable care must be exercised in discussing the magnitudes of $a_{\text{vinyl}}^{\text{H}}$ and $a_{\text{CH}_3}^{\text{H}}$ for methyl substituted vinyl groups.[15,17]



37

38

The values of $a_{7a}^{\text{H}}$ and $a_{7s}^{\text{H}}$ for **35** and **37** are both larger in magnitude than the corresponding values in **1**. The introduction of a double bond or benzo substituent was previously observed to have exactly the same effect in the bicyclo[2.2.2]octane-2,3-semidione system, *i.e.*, to increase magnitude of $a_{\text{anti}}^{\text{H}}$ and $a_{\text{syn}}^{\text{H}}$ by ~0.4 G. This effect is easily explained if $a_{\text{syn}}^{\text{H}}$ and $a_{\text{anti}}^{\text{H}}$ are both positive. For example it was previously suggested[24] that carbon–carbon hyperconjugation (**39**) could be facilitated by the presence of a double bond. Alternately, perhaps the introduction of double bond changes the geometry of the methylene group so that $a_{\text{anti}}^{\text{H}}$ becomes more positive and $a_{\text{syn}}^{\text{H}}$ more negative by nearly the same amount, a highly unlikely occur-

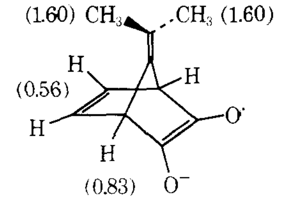


39

$n = 1, 2$

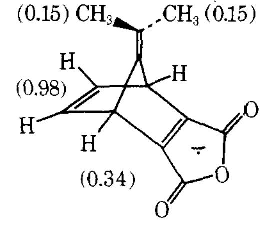
rence. The same effect is observed when the hfsc for 7-position of **5** and **36** are compared even though calculations indicate these hfs to be negative in sign. Of course in this case it is conceivable that the strain of the additional double bond simply increases the magnitude of the spin polarization interaction (**6**).

Semidione **40** and semifuraquinone **41** form an interesting pair of molecules with which to test the effect of the symmetry of the spin label.



**40**

$a^H$ in G

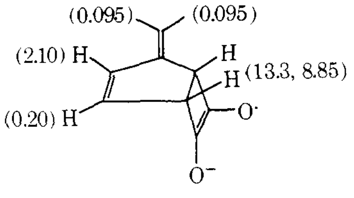


**41**

$a^H$ in G

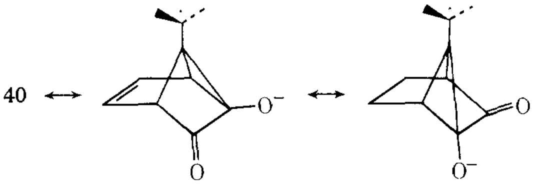
(see also ref. 17b)

Semidione **40** could be prepared by the electrolytic reduction of the dione while **41** was obtained by electrolysis of the dichloromaleic anhydride adduct of dimethylfulvene. Attempts to produce **40** from the *endo-* 3-*tert*-butyldimethylsiloxy 2-ketone by treatment with base in a flow system led only to the rearranged semidione **42.**[40] The hfsc's for **40** and **41** strongly support the concept of homoallylic conjugation when allowed by the symmetry of the HOMO of the spin label. Structures similar to **43** are not allowed for the semifuraquinone **41** because the isopropylidene group is in the nodal plane of this spin label.



**42**

$a^H$ in G



43

We have looked for homoallylic participation in semidione **44** where the hexadiene ring should also be constrained in a chair-like conformation. Oxidation of the ketone[42] yielded **44** which gave an esr spectrum with broad lines (0.5 G). The values of $a_\alpha{}^H$ require conformational stability for the cyclohexadiene ring of **44.** Whether the broadness of the lines was due to exchange by virtue of a ring flip or to unresolved hfs was not investigated. The magnitude of $a^H$ for the pseudo-equatorial hydrogen atom in **44** seems to agree fairly well with $a_b{}^H$ observed in the bicyclo[2.2.1]heptenesemidiones. The dihedral angle between this carbon-hydrogen bond and the semidione spin label is obviously greater in **44** than in **1** or **35.**

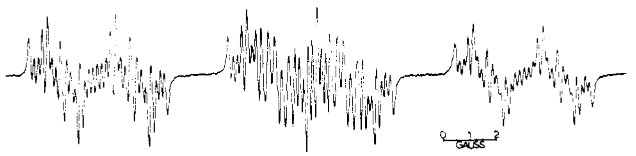
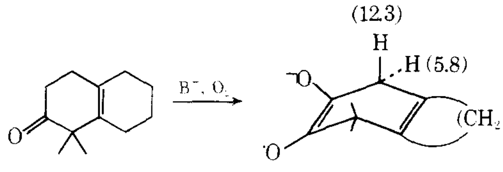


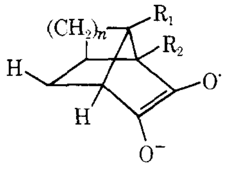
**Figure 4.** First derivative esr spectrum of semidione **45** in DMSO at 25°.



**44**

$a^H$ in G

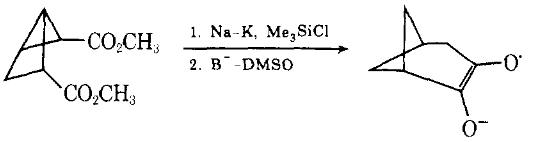
The effect of bridging between C-7 and C-5 in structure **1** could also have a considerable effect on the dihedral angle between the bridgehead hydrogen atom and the π-system. Oxidation of carvone camphor[43] yielded **45b,** with $a^H \simeq 2.8(2)$ G assigned to the bridgehead and *exo-* C-6 positions.



**45a,** $n = 0$ ; $R_1 = R_2 = H$

b, $n = 1$; $R_1 = R_2 = CH_3$

Attempts to prepare **45a** *via* acyloin condensation led to reductive ring opening of the cyclopropane ring.[21b]



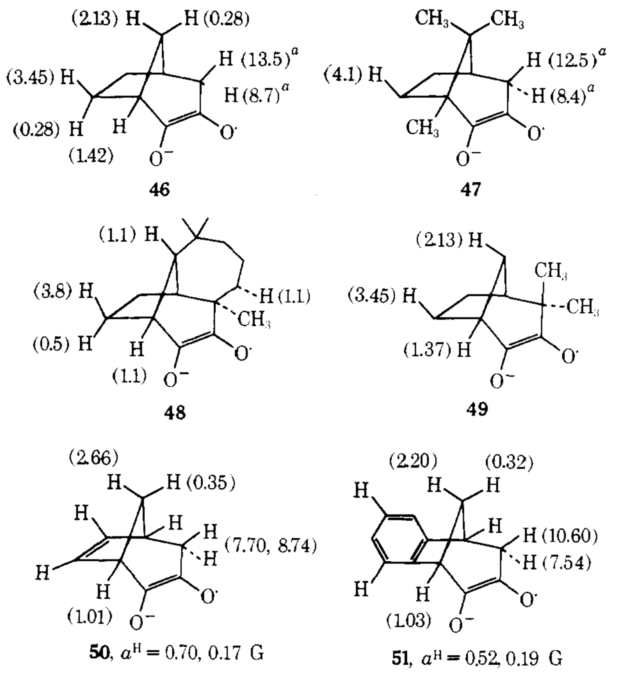
**Bicyclo[3.2.1]octane-2,3-semidiones.** In contrast to the bicyclo[2.2.1]heptane system, bicyclo[3.2.1]octan-2-one,[44] homocamphor,[45] bicyclo[3.2.1]oct-6-en-3-one,[46] and benzobicyclo[3.2.1]oct-6-en-3-one[47] were easily oxidized in basic solution to the 2,3-semidiones while longidione[48] and carbocamphenilone[49] were reduced to the semidione by base in DMSO. The bicyclo[3.2.1]octane-2,3-semidiones were stable in DMSO at 25° for hours. A consistent pattern of hfs is presented in Chart I. Long range hfs by the anti hydrogen at C-8 and the exo hydrogen at C-7 is noted and there appears to be spin delocalization by spin transfer or spin polarization. A typical highly resolved esr spectrum for **50** is given in Figure 4.

The strong long range hfs of the exo hydrogen at C-7 in **46–49** is particularly noteworthy. This suggests that the major unassigned hfsc in **50** and **51** result from homoallylic interactions, *i.e.,* **52** and **53.**

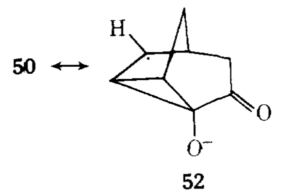
**Bicyclo[4.2.1]nonanesemidiones.** The 2,3-semidione in the bicyclo[4.2.1]nonane system has not been investigated. Bicyclo[4.2.1]nonane-3,4-semidione, **54,** is a conformationally mobile system which will be described in the future.[50]

Five tricyclic and three pentacyclic derivatives of **54** (all rigid) containing the cyclobutanesemidione ring have been described elsewhere.[26b]

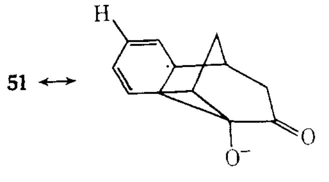
**Chart I.** $a^H$ in G



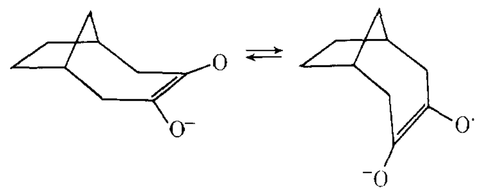
[a] Replaced by $a^D \simeq a^H/7$ in DMSO-$d_6$.



52



53



54

## Experimental Section

**Esr Spectra.** The procedure for the preparation of semidiones from ketones, α-hydroxy ketones, diketones, and bis(trimethylsiloxy)alkenes have been given previously.[26-28] The solutions of semidiones were examined at 25° with either a Varian Associates E-3 or V-4500 spectrometer using a V-4548 aqueous solution cell. *g*-Values were measured as 2.00497 for **1i** and 2.00483 for **1j**.[51] Semifuraquinones **29, 30,** and **41** were prepared by electrolysis of the dichloromaleic anhydride adducts in DMSO.[17]

**Bicyclo[2.2.1]hept-2-ene Oxide.** The oxide was prepared[51] by the reaction of 40% peracetic acid in chloroform with norbornene (Aldrich Chemical Co.) in the presence of sodium acetate, bp 153–157° (lit.[52] 155–158°).

**Dimethyl *cis*-1,3-Cyclopentanedicarboxylate. Precursor of 2 and 1a.** Norbornene (2.4 g), sodium carbonate (5.0 g), and acetone (200 ml) were stirred at 0° while solid potassium permanganate was added in small portions until a purple color persisted for more than 0.5 hr. The mixture was filtered by suction and the brown solid obtained was mixed with water (100 ml) and treated with sulfur dioxide until a clear solution was obtained. This solution was acidified with sulfuric acid and concentrated at reduced pressure to a white paste which was thoroughly extracted with diethyl ether. The combined ether washings were evaporated to yield 4.15 g (82%) of diacid, mp 117–119° (lit.[53a] mp 121.5°). The diacid was dissolved in methanol (50 ml) containing 5 drops of 96% sulfuric acid. After refluxing for 10 hr, the solution was evaporated to an oil which was taken up in ether and treated with 5% aqueous sodium bicarbonate until neutral. Distillation of the ether solution gave 96% of diester: bp 95–97° (1 Torr) (lit.[53b] bp 138–138.5 (25 Torr)), ir (neat) 1726 cm$^{-1}$; pmr (CCl$_4$) $\delta$ 1.8–3.0 (m, 8), 3.60 (s, 6).

**Dimethyl *trans*-4,*trans*-5-Dideuterio-*r*-1,*cis*-3-cyclopentanedicarboxylate. Precursor to 1d.** *exo,cis*-5,6-Dideuterionorbornene was prepared from the partial reduction of norbornadiene (Aldrich Chemical Co.) with deuterium (Matheson Chemical Co.) according to the literature.[54] The diester was prepared by potassium permanganate oxidation of this olefin by the same procedure previously given for norbornene.

**Dimethyl *trans*-2-Deuterio-*cis*-1,3-cyclopentanedicarboxylate. Precursor to 1b.** *anti*-7-Hydroxynorbornene[55] (7.0 g) was dissolved in 50 ml of pentane. This solution was shaken for 10 min at 25° with 100 ml of 47–49% hydrobromic acid. The layers were separated, and the pentane solution was washed with water (15 ml), dried (MgSO$_4$), and concentrated to an oil which yielded 5.5 g of *anti*-7-bromonorbornene upon distillation: bp 63–65° (20 Torr); pmr (CCl$_4$) $\delta$ 1.04 (m, 2), 2.04 (m, 2), 2.75 (m, 2), 3.74 (m, 1), and 6.03 (t, 2, $J$ = 2.2 Hz). The bromide (3.0 g) was mixed with diglyme-D$_2$O (32 ml, 65% diglyme-35% D$_2$O), 2.0 g sodium borodeuteride (Merck Sharp and Dohme of Canada, Ltd.), and 0.16 g of sodium hydroxide and stirred at 50° for 2 hr under nitrogen. The mixture was diluted with 100 ml of water and extracted with pentane (3 × 40 ml). The combined extracts were dried (MgSO$_4$) and combined with 250 ml of acetone. This solution was treated with potassium permanganate as previously described. The diacid thus obtained was converted to the diester by refluxing in methanol with a trace of sulfuric acid. The diester (1.15 g) was purified by preparative glpc (15% Carbowax 20M on Chromosorb W, 160°): pmr (CCl$_4$) $\delta$ 1.7–2.2 (m, 4), 2.4–3.1 (m, 1), and 3.61 (s, 6).

**7-Deuteriobicyclo[2.2.1]hept-2-ene (syn/anti mixture). Precursor of 1b and 2c.** *syn*-7-Bromobicyclo[2.2.1]hept-2-ene[56] (2.4 g) and tri-*n*-butyltin deuteride (prepared from 7.0 g of tri-*n*-butyltin chloride (Columbia Chemical Co.) and 0.5 g of lithium aluminum deuteride (Metal Hydrides Inc.))[57] were mixed with 10 ml of hexane and allowed to stand at room temperature for 24 hr. The hexane was carefully distilled at atmospheric pressure. The residue was heated to 150° at 1 Torr and 80 mg of 7-deuteriobicyclo[2.2.1]hept-2-ene was collected in a cold trap at −78°. An additional 800 mg of olefin was isolated from the hexane distillate by preparative glpc (20% TCEP, 40°). The olefin was shown to contain both *syn*- and *anti*-7-deuteriobicyclo[2.2.1]hept-2-ene (83% anti, 17% syn) by analysis of the esr spectrum of the resulting semidiones.[58]

**7,7-Dimethoxybicyclo[2.2.1]heptan-2-one. Precursor of 1e.** The ketone was prepared from the Diels–Alder adduct of it 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene[59a] and ethylene as described in the literature.[59b,c]

**1,4-Dideuterio-7,7-dimethoxybicyclo[2.2.1]heptan-2-one. Precursor of 1f.** This ketone was prepared by the same reactions as the precursor to **1e** except the O-deuterated *tert*-butyl alcohol (96.4% by nmr) was employed in the dechlorination reaction of the Diels–Alder adduct of 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene and ethylene.

**1-Methylbicyclo[2.2.1]heptane-2,3-dione. Precursor of 1g.** Norcamphor was converted to 2-methyl-2-norborneol which in acetic acid at 60° yielded 1-methyl-2-norbornyl acetate.[60] Hydrolysis by ethanolic potassium hydroxide gave 1-methyl-2-norborneol, mp 72–75°, bp 84° (20 Torr). Treatment of 11 g of 1-methyl-2-norborneol in 10 ml of glacial acetic acid with a solution of 6.5 g of chromium trioxide in 6.5 ml of acetic acid and 4 ml of water gave after 5 hr 7.5 g of 1-methylnorcamphor isolated by distillation of the ether extract: bp 63–65° (15 Torr); ir 1740 cm$^{-1}$. A mixture of 10.1 g of 1-methylnorcamphor and 9.0 g of selenium dioxide in 30 ml of xylene was refluxed with stirring for 4 hr. The solution was cooled and filtered, and the xylene was distilled at 20 Torr. Sublimation of the residue under vacuum gave 4.5 g of the dione, mp 50-54°.

**7-Methylbicyclo[2.2.1]hept-2-ene (syn and anti).**[61] *syn*-7-Bromo-*anti*-7-methylbicyclo[2.2.1]hept-2-ene[62] (41 g) was mixed with tri-*n*-butyltin hydride (prepared from 52 g of tri-*n*-butyltin chloride and 3.0 g of lithium aluminum hydride).[56] The reaction was very exothermic initially. After 15 hr at room temperature additional tri-*n*-butyltin hydride was added (prepared from 26 g of tri-*n*-butyltin chloride). After a second 15 hr period, the mixture was distilled to yield 19.5 g (83%) of 7-methylnorbornenes, bp 27-30° (50 Torr). Pmr analysis indicated that the product contained 55% of the *anti*-7-methyl isomer and 45% of the syn.

**7-Methylbicyclo[2.2.1]heptan-2-one (syn and anti).**[61] Sodium borohydride (0.9 g, 24 mmol), 0.2 g of anhydrous zinc chloride, 5.0 g (46.3 mmol) of 7-methylnorbornene (syn and anti), and 10 ml of ethyl ether were mixed under nitrogen and cooled to 0° in an ice bath. Boron trifluoride etherate (11.4 g, 80 mmol) was slowly added over a 1-hr period. After 6 hr, the excess diborane was decomposed with 5 ml of water. A solution of 11.0 g (36.9 mmol) of sodium dichromate dihydrate, 8.25 ml of 96% sulfuric acid, and 30 ml of water was added and the mixture was refluxed for 2 hr. The layers were then separated and the aqueous layer was extracted with ether (3 × 50 ml). The combined ether extracts were dried ($MgSO_4$) and distilled to give 2.75 g of a mixture of *syn*- and *anti*-7-methylbicyclo[2.2.1]hept-2-one: bp 95-105° (45 Torr); pmr ($CCl_4$) $\delta$ 1.94 (d, $J = 6.6$ Hz), 1.95 (d, $J = 7$ Hz), 1.1-2.4 (overlapping multiplets); ir (neat) 1740 $cm^{-1}$.

***syn*-7-Methylbicyclo[2.2.1]heptan-2,3-dione. Precursor of 1j.** 7-Methylbicyclo[2.2.0]heptan-2-one, present in 0.8 g of the syn-anti mixture, 0.8 g (7.2 mmol) of selenium dioxide, and 10 ml of xylene were mixed and vigorously refluxed for 6 hr. The mixture was filtered and the filtrate was chromatographed over silica gel using pentane (70%)-benzene (30%), then pentane (80%)-chloroform (20%), and finally methanol as eluents. A 70-ml fraction of the methanol eluate contained the yellow $\alpha$-diketone. This fraction was evaporated at reduced pressure to 10 ml, diluted with 50 ml of pentane, and washed with water (2 × 25 ml). The layers were separated, and the pentane layer was dried ($MgSO_4$) and evaporated to a yellow oil which solidified upon cooling to −21°. The yellow solid was recrystallized from benzene (50%)-hexane (50%) to yield 118 mg (26%) of the $\alpha$-diketone: mp 73-74°; ir (KBr) 1778 and 1754 $cm^{-1}$; pmr ($CDCl_3$) $\delta$ 1.10 (d, 3, $J = 7.5$ Hz), 1.5-2.8 (m, 5), 2.89 (m, 2); mass spectrum (70 eV) *m/e* 138 (parent ion), 110.[63]

**Dimethyl *trans*-2-Methylcyclopentane-*cis*-1,3-dicarboxylate. Precursor of 1h.** 7-Methylbicyclo[2.2.1]hept-2-ene (3.0 g of the syn-anti mixture) was oxidized with potassium permanganate in acetone to yield 2.75 g (57%) of a mixture of diacids. The diacid mixture (606 mg) was refluxed with 10 ml of 50% sulfuric acid for 8 hr before the solution was extracted with ether (5 × 10 ml). The combined ether extracts were dried ($MgSO_4$) and then evaporated to yield a white solid. The solid was recrystallized from ethyl acetate at −21° to yield 273 mg (45%) of pure *trans*-2-methyl-*cis*-1,3-cyclopentanedicarboxylic acid, mp 152-153° (lit.[64] mp 154-155°). The diacid was converted to the dimethyl ester by refluxing in methanol and a trace of sulfuric acid: ir (neat) 1730 $cm^{-1}$; mass spectrum (70 eV) *m/e* 200 (parent ion), 185, 169, 140.

**7-Carbomethoxybicyclo[2.2.1]hept-2-ene (syn and anti).** Ethylene bromide (100 g, 0.53 mol) was added under nitrogen over a 5-hr period to a mixture of 52.3 g (0.31 mol) of *syn*-7-bromobicyclo[2.2.1]hept-2-ene, 20.2 g (0.84 mol) of magnesium, and 450 ml of ethyl ether. After stirring for 5 days, dry carbon dioxide was bubbled through the mixture for 1 hr. The mixture was hydrolyzed with 300 ml of 6 *N* hydrochloric acid and extracted with ether (5 × 50 ml). The combined ether extracts were dried ($Na_2SO_4$) and evaporated to give 29.6 g (44%) of a carboxylic acid mixture which yielded 21.7 g of methyl ester upon refluxing in 150 ml of methanol and 2 ml of 96% sulfuric acid, bp 68-75° (5 Torr) (lit.[65] syn bp 95.5 (25 Torr), anti bp 93-93.5° (30 Torr)).

**Trideuteriomethylbicyclo[2.2.1]hept-2-ene (syn and anti).** 7-Carbomethoxybicyclo[2.2.1]hept-2-ene (8.0 g of the syn-anti mixture) was reduced to 7-$\alpha,\alpha$-dideuteriomethanolbicyclo[2.2.1]hept-2-enes by treatment with 1.3 g of lithium aluminum deuteride (Metal Hydrides Corp.) in 90 ml of ethyl ether. The crude alcohol mixture was converted to a mixture of tosylates by mixing with 10 g of *p*-toluenesulfonyl chloride in 35 ml of pyridine at 0° for 24 hr. The pyridine mixture was diluted with 200 ml of 6 *N* hydrochloric acid at 0° to yield 10.9 g (68% overall yield) of the tosylate: mp 45-48° (from methanol) (lit.[65] syn, mp 38.5-39.5°, anti, mp 60-61°); pmr ($CDCl_3$) $\delta$ 1.73-1.97 (m, 5), 2.44 (s, 3), 2.66 (m, 2), 5.76 (t, 1.1, $J = 2$ Hz, vinyl H of anti isomer), 7.33 (d, $J = 8.5$ Hz), and 7.77 (d, $J = 8.5$ Hz). This tosylate mixture was dissolved in 60 ml of ether and added over a 0.5-hr period to a solution of 0.7 g of lithium aluminum deuteride in 140 ml of ether. The reaction mixture was refluxed for 2 days and hydrolyzed with saturated aqueous sodium chloride and the ether was decanted and dried ($MgSO_4$). After the ether was carefully distilled, the residue was heated to 100° (1 Torr) and the 7-trideuteriomethylbicyclo-[2.2.1]hept-2-ene was collected in a cold trap (−78°): pmr ($CCl_4$) $\delta$ 0.7-1.3 (m, 2), 1.43-1.83 (m, 3), 2.38 (m, 1.2), 2.50 (m, 0.8), 5.79 (m, 0.8), and 5.98 (t, 1.2, $J = 2$ Hz).

**Dimethyl *trans*-2-Trideuteriomethyl-*cis*-1,3-cyclopentanedicarboxylate. Precursor of 1i.** The mixture of *syn*- and *anti*-7-trideuteriomethylbicyclo[2.2.1]hept-2-enes was oxidized with potassium permanganate in acetone and the crude diacid (mp 137-142°) was converted to pure dimethyl *trans*-2-trideuteriomethyl-*cis*-1,3-cyclopentanedicarboxylate by refluxing in methanol and a trace of sulfuric acid. This diester was purified by preparative glpc (15% Carbowax 20M on Chromosorb W, 160°): ir (neat) 2210, 1728 $cm^{-1}$; pmr ($CCl_4$) $\delta$ 1.8-2.5 (m, 2) and 3.64 (s, 6); mass spectrum (70 eV) *m/e* 203 (parent ion), 185, 1972, 143.

**1,7-*syn*-Dimethyl-2-norbornanone ($\beta$-Santenone). Precursor of 1k.** Isosantene (exo and endo isomers) was prepared from 3-methylnorcamphane-2-methanol,[66] bp 137-140°. Treatment of the isosantene with acetic acid and a trace of 96% sulfuric acid yielded a mixture of acetates which were hydrolyzed with ethanolic potassium hydroxide to $\alpha$- and $\beta$-santenol, mp 84-87°.[67] To the santenol isomers (3 g) in 1.6 ml of glacial acetic acid was added dropwise a solution of chromium trioxide (1.5 g) in 1.5 ml of acetic acid and 0.9 ml of water. After stirring for 9 hr the solution was diluted with water and extracted with ether. The ether extracts were washed with saturated aqueous $NaHCO_3$ and dried over $Na_2SO_4$. Removal of the other left an oil which was separated by glpc. $\beta$-Santenone had the lowest retention time and gave a pmr ($CCl_4$) showing methyl groups at $\delta$ 1.66 (s) and 1.46 (d), semicarbazone mp 224-226° (lit.[68] mp 223-224°). The $\alpha$-santenone gave a pmr ($CCl_4$) showing methyl groups at $\delta$ 1.66 (s) and 1.80 (d), semicarbazone mp 205-210° (lit.[66] mp 235-236°).

**1,7-*syn*-Dimethylbicyclo[2.2.1]heptane-2,3-dione** was prepared by oxidation of 4 g of ~1:1 mixture of $\alpha$- and $\beta$-santenones by 3.2 g of selenium dioxide in 20 ml of refluxing xylene for 4 hr. The cold reaction mixture was filtered, the xylene was distilled at 20 Torr, and the residue was sublimed under vacuum to give 1.31 g of material, mp 84-86°. Methyl singlets in the pmr spectrum ($CCl_4$) appeared at $\delta$ 1.09 and 1.14.

**Dimethyl *trans*-4,*trans*-5-Dimethyl-*r*-1,*cis*-3-cyclopentanedicarboxylate. Precursor of 1p.** *exo,cis*-5,6-Dimethylbicyclo-[2.2.1]hept-2-ene[69] (3.0 g) was dissolved in 75 ml of methanol and cooled to −78°. One equivalent of ozone (generated with a Welsbach ozone generator) was bubbled into this solution. The methanol was removed at reduced pressure and the residual oil was refluxed for 30 min with 15 ml of 90% formic acid and 8 ml of 30% hydrogen peroxide. This mixture was concentrated at reduced pressure to yield the crude diacid which yielded 2.8 g (53% overall) of the dimethyl ester upon refluxing in methanol and a trace of sulfuric acid. The diester was purified by preparative glpc (15% Carbowax on Chromosorb W, 160°): pmr ($CCl_4$) $\delta$ 0.93 (d, 61, $J = 6.0$ Hz), 1.9-2.6 (m, 6), and 3.62 (s, 6).

***endo,cis*-5,6-Dimethylbicyclo[2.2.1]heptan-*exo*-2-ol.** *endo,cis*-5,6-Dimethylbicyclo[2.2.1]hept-2-ene (1.2 g) was mixed with 0.4 g of sodium borohydride in 5 ml of diglyme under nitrogen at 0°. A solution of 1.8 g of boron trifluoride etherate in 5 ml of diglyme was added over a 1-hr period. This mixture was stirred for 2 hr at room temperature then the excess diborane was destroyed by the careful addition of 2 ml of water. This mixture was oxidized by the addition of 5 ml of 3 *N* sodium hydroxide and 5 ml of 30% hydrogen peroxide. After 1 hr, the mixture was diluted with 250 ml of ice water and extracted with ether (2 × 50 ml). The combined ether extracts were dried ($Na_2SO_4$) and evaporated to an oil which was distilled to yield 1.7 g (83%) of the alcohol: bp 130-128° (55 Torr); ir (neat) 3620 and 3390 $cm^{-1}$.[63]

***endo,cis*-5,6-Dimethylbicyclo[2.2.1]heptan-2-one.** A solution of 1.7 g of chromium trioxide, 3 ml of water, and 15 ml of glacial acetic acid was added dropwise over a 1-hr period to a solution of 4.9 g of *endo,cis*-5,6-dimethylbicyclo[2.2.1]heptan-2-one in 15 ml of glacial acetic acid. After 8 hr the mixture was diluted with 300 ml of ice water and extracted with ether (5 × 70 ml). The combined ether extracts were washed until neutral with 5% sodium bicarbonate, dried ($Na_2SO_4$), and concentrated to an oil which yielded 3.2 g (66%) of a waxy solid upon distillation: bp 103–106 (13 Torr); ir ($CCl_4$) 1744 cm$^{-1}$.[63]

*endo,cis*-**5,6-Dimethylbicyclo[2.2.1]heptane-2,3-dione. Precursor of 1q.** A mixture of 3.20 g of *endo,cis*-5,6-dimethylbicyclo[2.2.1]heptane-2-one, 2.9 g of selenium dioxide, and 15 ml of xylene was refluxed for 4 hr. The mixture was filtered and distilled to yield 1.62 g (46%) of a yellow oil which solidified on standing, bp 135–140° (35 Torr). The solid was purified by sublimation at 75° (5 Torr) to yield bright yellow crystals, mp 87–91°. An analytical sample was prepared by column chromatography over 20 mesh silica gel using pentane (200 ml), then pentane (50%)–benzene (50%) until a yellow fraction was collected. Evaporation of the solvent left a solid which was recrystallized from hexane to yield yellow crystals: mp 101–102°; ir ($CCl_4$) 1781 and 1762 cm$^{-1}$; pmr ($CCl_4$) $\delta$ 0.88 (d, 6, $J$ = 6.9 Hz), 2.11 (m, 2), 2.67 (m, 2), and 2.85 (m, 2); mass spectrum (70 eV) *m/e* 152 (parent ion), 124, 95, 81, and 69.[63]

**Dimethyl Octahydro-*cis*-pentalene-*trans*-1,*trans*-3-dicarboxylate. Precursor of 31.** *exo*-8-Ketotricyclo[5.2.1.$0^{2,6.}$]decane (8.2 g, Aldrich Chemical Co.) was mixed with 75 ml of concentrated nitric acid. This mixture was heated on a steam bath for 3 hr, diluted with 150 ml of water, and cooled to 0° to yield 2.4 g (22%) of diacid, mp 173–175°; recrystallized from ethyl acetate–hexane, mp 180–181° (lit.[70] mp 182.5–183°). The diester was obtained by refluxing a solution of the diacid in methanol containing a trace of sulfuric acid. The diester was purified by preparative glpc (15% Carbowax 20M on Chromosorb W, 180°): pmr ($CCl_4$) $\delta$ 1.57 (m, 6), 1.7–2.9 (m, 6), and 3.62 (s, 6).

**Dimethyl Octahydro-*cis*-pentalene-*cis*-1,*cis*-3-dicarboxylate. Precursor of 32.** *endo*-8-Ketotricyclo[5.2.1.$0^{2,6}$]decane[71] (3.55 g) was stirred at room temperature for 2 days with a mixture of 7.5 g of potassium permanganate, 2.0 g of potassium hydroxide, and 100 ml of water. Work-up in the same manner as previously described for permanganate oxidations yielded 100 mg (2%) of the diacid, mp 227–229° (lit.[70] mp 231.5–232°). Refluxing a methanol solution of the diacid yielded 85 mg (74%) of the dimethyl ester which was purified by preparative glpc (15% Carbowax 20M on Chromosorb W, 180°); pmr ($CCl_4$) $\delta$ 1.2–2.9 (m, 12) and 3.62 (s, 6); mass spectrum (70 eV) *m/e* 226 (parent ion), 195, 194, 166, 155, 126, and 67.

*endo*-**Tricyclo[3.2.1.$0^{2,4}$]oct-6-ene.** The tricyclic olefin was prepared by the literature procedure[72]: pmr $\delta$ 0.20–0.75 (m, 2), 1.15–1.45 (m, 2), 1.6–1.9 (m, 2), 2.6–2.9 (m, 2), 5.55–5.75 (t, 2, $J$ = 1.9 Hz).

**Dimethyl Bicyclo[3.1.0]hexane-*endo,cis*-2,4-dicarboxylate. Precursor of 15.** A solution of 4.9 g of *endo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene in 300 ml of acetone was stirred and cooled at 0° while 18.3 g of potassium permanganate was added slowly over a 6-hr period. The solution was allowed to warm slowly to room temperature, stirred for an additional 10 hr, and filtered. The filter cake was added to 250 ml of water and sulfur dioxide was bubbled through the stirred suspension until no manganese dioxide remained. The solution was acidified to Congo Red with 50% sulfuric acid and extracted with three 100-ml portions of ether. The combined ether extracts were evaporated to 50 ml and extracted with three 20-ml portions of 10% aqueous $NaHCO_3$ and the extracts were acidified to Congo Red. The aqueous acid solution was extracted with three 100-ml portions of ethyl acetate and the extracts were dried ($MgSO_4$) before filtering and evaporation under reduced pressure to give the crude diacid. The diacid was dissolved in 25 ml of methanol and treated with an ethereal solution of diazomethane until the characteristic color persisted. Removal of the solvent under reduced pressure gave 2.3 g (25%) of the diester purified by glpc (15% Carbowax 20M column at 190°): ir (neat) 1730 cm$^{-1}$; pmr ($CCl_4$) $\delta$ 0.20–0.90 (m, 2), 1.40–2.05 (m, 4), 2.75–3.25 (m, 2), 3.65 (s, 6); mass spectrum (70 eV) *m/e* (rel intensity) = 198 (parent ion, 20), 167 (18), 139 (100).

*exo*-**Tricyclo[3.2.1.$0^{2,4}$]oct-6-ene.** To a warm solution of cupric acetate (0.5 g of monohydrate) in 50 ml of glacial acetic acid was added 35 g of zinc (30 mesh). The mixture was shaken for 3 min while warm. The liquid was decanted and the residue was washed with 50 ml of acetic acid and three 50-ml portions of ether. Ether (100 ml) and a few milliliters of methylene iodide were added to the couple, and the mixture was refluxed as 24 g of bicyclo[2.2.1]heptadiene and 59 g of methylene iodide were added dropwise for 90 min. The mixture was refluxed 20 hr before cooling. The liquid was decanted into a separatory funnel containing ice and 1 *N* hydrochloric acid. The ether layer was separated and washed with another 50 ml of acid and with saturated aqueous $NaHCO_3$ before drying and distillation to give 16.4 g (59%) of product which was analyzed to be a 3:1 exo:endo ratio of isomers by pmr. The exo isomer had a pmr ($CCl_4$) $\delta$ 0.6–1.10 (m, 4), 1.15–1.50 (m, 2), 2.60–2.80 (m, 2), and 6.25–6.40 (t, 2, $J$ = 1.9 Hz).

**Dimethyl Bicyclo[3.1.0]hexane-*exo,cis*-2,4-dicarboxylate. Precursor to 14.** A 13.4-g sample of the above olefin mixture was oxidized with 65 g of potassium permanganate and converted to the diesters using the procedure for the preparation of the precursor to **15.** A 6.2-g (24%) mixture of the diesters was obtained which was separated by glpc using a 5 ft × 0.25 in. Carbowax 20M column at 170°. The exo isomer had the longest retention time: ir (neat) 1730 cm$^{-1}$; pmr ($CCl_4$) $\delta$ 0.00–0.80 (m, 2), 1.25–1.85 (m, 3), 2.25–2.55 (d, 1, $J$ = 14.5 Hz), 2.60–2.83 (d, 2, $J$ = 8 Hz), 3.60 (s, 6); mass spectrum (70 eV) *m/e* (rel intensity) 198 (parent ion, 30), 167 (33), 139 (100).

**Dimethyl Tetracyclo[4.3.0.$0^{2,4}$.$0^{3,7}$]nonane-*endo,cis*-8,9-dicarboxylate.** Dimethyl tetracyclo[4.3.0.$0^{2,4}$.$0^{3,7}$]non-8-ene-8,9-dicarboxylate was obtained by refluxing equimolar amounts of norbornadiene and dimethyl acetylenedicarboxylate,[73] mp 66–67° (lit.[74] mp 64°). Hydrogenation in benzene in the presence of 10% palladium on charcoal gave the saturated ester: mp 64–66° (lit.[73] mp 61–62°); pmr ($CCl_4$) $\delta$ 1.10–1.35 (m, 3), 1.48 (t, 2, $J$ = 1 Hz), 1.79 (broad s, 1), 2.21 (broad s, 2), 3.08 (t, 2, $J$ = 1.5 Hz), 3.57 (s, 6); mass spectrum (70 eV) *m/e* (rel intensity) 236 (parent ion, 40), 205 (25), 177 (15).

**Tetracyclo[4.3.0.$0^{2,4}$.$0^{3,7}$]non-8-ene.** Lead tetraacetate (73 g) and 17.5 g of tetracyclo[4.3.0.$0^{2,4}$.$0^{3,7}$]nonane-*endo,cis*-8,9-dicarboxylic acid were mixed with 250 ml of pyridine, and the mixture was degassed for 10 min with oxygen. The mixture was heated to 76° in an oil bath whence the reaction began and quickly subsided. After standing an additional 5 min the mixture was cooled and poured into a cool solution of 250 ml of nitric acid in 1250 ml of water and was extracted three times with 600 ml of ether, the ether was washed twice with 150 ml of saturated aqueous $NaHCO_3$, and after evaporation of the ether the product was purified by bulb-to-bulb distillation under vacuum to give 1.55 g of the pure olefin: pmr ($CCl_4$) $\delta$ 1.03–1.28 (d, 2, $J$ = 5 Hz), 1.47–1.60 (t, 2, $J$ = 1.9 Hz), 1.60–1.80 )m, 1), 1.80–2.00 (m, 1), 2.47–2.64 (m, 2), 5.92–6.02 (t, 2, $J$ = 1.9 Hz).

**Dimethyl Tricyclo[2.2.1.$0^{2,6}$]heptane-*endo,endo*-3,5-dicarboxylate. Precursor of 16.** Oxidation of 1.4 g of the above olefin with 6.2 g of potassium permanganate gave 0.95 g of the solid diester. Purification by glpc (10% QF-1 column at 170°) gave material: mp 80.5–81.5°; ir ($CCl_4$) 1730 cm$^{-1}$; pmr ($CCl_4$) $\delta$ 1.15–1.60 (m, 5), 2.33–2.45 (m, 2), 2.50–2.67 (m, 1), 3.54 (s, 6); mass spectrum (70 eV) *m/e* (rel intensity) 210 (parent ion, 4), 179 (25), 151 (24).

**1,7,7-Trimethylbicyclo[2.2.1]heptadiene.** Using a modification of a literature method[75] 25 g of *endo,endo*-2,6-dichloro-1,7,7-trimethylbicyclo[2.2.1]heptane[76] was added to a solution of 6.5 g of sodium in 100 g of 1-nonanol that had been heated to 245° and the diolefin was collected. Material purified by glpc had mp 101–102° (lit.[75] 103–103.5°) and pmr ($CCl_4$) $\delta$ 1.01 (s, 6), 1.20 (s, 3), 2.90–3.10 (m, 1), 6.20–6.35 (d, d, 2, $J$ = 5.4, 1.3 Hz), 6.45–6.65 (d, d, 2, $J$ = 5.4, 3.3 Hz).

**Dimethyl 4,5,5- (and 5,5,6-) Trimethyltetracyclo[4.3.0.-$0^{2,4}$.$0^{3,7}$]nonane-*endo,cis*-8,9-dicarboxylate.** 1,7,7-Trimethylbicyclo[2.2.1]heptadiene (23 g) and maleic anhydride (18 g) were heated in 7 ml of xylene at 190° for 16 hr. Removal of the xylene under vacuum and recrystallization from ethyl acetate gave 4.5 g of a pure isomer: mp 159–161°; pmr ($CDCl_3$) $\delta$ 0.84 (s, 3), 0.86 (s, 6), 1.20–1.30 (m, 3), 2.33–2.48 (m, 2), 3.45 (quartet, $J$ = 1.9, 3.2 Hz). Esterification with boron trifluoride–methanol complex gave the diester: nmr ($CCl_4$) $\delta$ 0.78 (s, 3), 0.80 (s, 6), 1.02 (t, 1, $J$ = 5 Hz), 1.35 (d, 2, $J$ = 5.0 Hz), 2.07 (m, 2), 3.02 (m, 2), 3.59 (s, 6); mass spectrum (70 eV) *m/e* (rel intensity) 278 (100), 247 (33), 219 (15). The nmr was indicative of the 5,5,6-trimethyl isomer.

The mother liquors from the recrystallization were evaporated to leave a semisolid residue which was eluted from a silica gel column by benzene (50%)-pentane (50%). Esterification gave a mixture which could be separated into four substances by glpc (15% FFAP, 210°). The first and fourth peaks were not identified while the third peak was the 5,5,6-trimethyl isomer. The second and largest peak was identified as the 4,5,5-trimethyl ester: mp 45–52°; pmr ($CCl_4$) δ 0.85 (s, 6), 1.01 (s, 3), 1.16 (m, 2), 1.42 (m, 1), 2.47 (m, 2), 3.00 (t, 2, *J* = 2.0 Hz), 3.57 (s, 6); mass spectrum (70 eV) *m/e* (rel intensity) 278 (20), 247 (12), 219 (6).

**5,5,6-Trimethyltetracyclo[4.3.0.0$^{2,4}$.0$^{3,7}$]non-8-ene.** 5,5,6-Trimethyltetracyclo[4.3.0$^{2,4}$.0$^{3,7}$]nonane-*endo,cis*-8,9-dicarboxylic anhydride (4.1 g) and 6 g of sodium carbonate were heated to 50° for 12 hr in 100 ml of water. Following neutralization with hydrochloric acid the diacid was isolated by filtration to give 4.3 g of material which was bisdecarboxylated with lead tetraacetate (as described in the synthesis of precursors to **16**) to give 540 mg of the olefin: pmr δ 0.60 (s, 3), 0.80 (s, 6), 1.16–1.33 (d, 2, *J* = 4.8 Hz), 1.50–1.70 (t, 1, *J* = 4.8 Hz), 2.30–2.45 (m, 2), 5.92–6.03 (t, 2, *J* = 2.0 Hz).

**Dimethyl 4,7,7-Trimethyltricyclo[2.2.1.0$^{2,6}$]heptane-*endo,endo*-3,5-dicarboxylate. Precursor of 17.** Oxidation of 0.5 g of 5,5,6-trimethyltetracyclo[4.3.0.0$^{2,4}$.0$^{3,7}$]non-8-ene with potassium permanganate in acetone gave 350 mg of solid diacid which was esterified with the boron trifluoride–methanol complex to give 80 mg of diester purified by glpc (10% QF-1 column, 175°) to give material: mp 70–73°; pmr ($CCl_4$) δ 0.90 (s, 6), 0.98–1.23 (m, 1), 1.25 (s, 3), 1.50–1.67 (d, 2, *J* = 5.3 Hz), 2.53 (s, 2), 3.59 (s, 6); mass spectrum (70 eV) *m/e* (rel intensity) 252 (parent ion, 1), 221 (33), 193 (16).

**Dimethyl 1,7,7-Trimethyltricyclo[2.2.1.0$^{2,6}$]heptane-*endo,endo*-3,5-dicarboxylate. Precursor to 18.** Treatment of the mixture of anhydrides from the reaction of 1,7,7-trimethylbicyclo[2.2.1]heptadiene and maleic anhydride as described for the pure 5,5,6-trimethyltetracyclo[4.3.0$^{2,4}$.0$^{3,7}$]nonane-*endo,cis*-8,9-dicarboxylic anhydride gave a ∼1:1 mixture of the two olefins which were difficult to separate. The 4,5,5-trimethyltetracyclo[4.3.0.0$^{2,4}$.0$^{3,7}$]-non-8-ene had a pmr of δ 0.83 (s, 6), 1.04 (s, 3), 0.90–1.50 (m, 2), 2.65–2.85 (m, 2), and 5.88–6.00 (t, 2, *J* = 2.0 Hz). Oxidation of the olefin mixture as described for the pure 5,5,6-trimethyltetracyclo[4.3.0$^{2,4}$.0$^{3,7}$]non-8-ene followed by esterification gave a mixture of diesters in which the 1,7,7-trimethyl isomer predominated by nearly twofold. Separation of the isomers was achieved by glpc using a 10% QF-1 column at 170°. The pure ester had: mp 65.5–68.5°; ir ($CCl_4$) 1730 cm$^{-1}$; pmr ($CCl_4$) δ 0.95 (s, 6), 1.05 (s, 3), 1.33–1.43 (m, 2), 2.10–2.25 (m, 1), 2.75–2.85 (m? 2), 3.50 (s, 6); mass spectrum (70 eV) *m/e* (rel intensity) 252 (parent ion, 10), 221 (40), 193 (30).

**2,3-Dichloro-1,2,3,4-tetrahydro-1,4-(1,1-cyclopropano)phthalic Anhydride. Precursor to 29.** Spiro[2.4]-4,6-heptadiene[77] (9.2 g, 0.1 mol) and 16.7 g (0.1 mol) of dichloromaleic anhydride in 100 ml of benzene reacted over 1 week at room temperature. The benzene was distilled at 30° to give material which after recrystallization from acetic acid was purified on a silica gel column (hexane–chloroform eluent) to give 10.1 g (38%) of the desired anhydride: mp 113.5–115.0°; pmr ($CDCl_3$) δ 6.40–6.55 (m, 2), 2.80–3.01 (m, 2), 0.87–1.25 (m, 2), 0.24–0.65 (m, 2).

**1,2-Dichloro-3,6-(1,1-cyclopropano)cyclohexane-1,2-dicarboxylic Anhydride. Precursor to 30.** 2,3-Dichloro-1,2,3,4-tetrahydro-1,4-(1,1-cyclopropano)phthalic anhydride was hydrogenated in ethyl acetate with palladium–charcoal catalyst until 1 equiv of hydrogen had been absorbed (5 min). The solution was filtered and solvent was removed at 30° to give a product: mp 178.1–179.0° (recrystallized from acetic acid); pmr ($CHCl_3$) δ 1.10–2.35 (m, 6), 0.32–0.70 (m, 4).[63]

**Dimethyl Octahydro-*exo*-4,7-methanoindene-*cis,cis*-1,3-dicarboxylate. Precursor to 33.** The known dicarboxylic acid[78] was prepared by the oxidation of 1,2,3,4,4a,5,8,8a-octahydro-1,4,5,8-*exo,endo*-dimethanonaphthalene obtained from dihydroaldrin according to the literature procedure.[79] The olefin (1 g) was dissolved in 2500 ml of water containing 10.7 g of sodium periodate, 0.134 g of potassium permanganate, and potassium carbonate to give a pH of 7–8. After 10 hr at 25° the solution was concentrated to 200 ml, basicified, extracted with ether, acidified, and again extracted with ether. From the final extracts 100 mg of acid, mp 253–256 (lit.[77] mp 256°), was obtained. The diacid (90 mg) in methanol (20 ml) containing a trace of sulfuric acid was refluxed for 20 hr. The methanol was evaporated at 25° and the residue was dissolved in ether, washed with aqueous 10% sodium hydroxide, and dried over magnesium sulfate. Removal of the ether under vacuum gave 90 mg of material mp 94–95°, which gave only one peak in glpc (3% SE-30, 162°): pmr ($CCl_4$) δ 0.85–3.0 (m, 14), 3.68 (s, 6).

**Dimethyl Octahydro-*endo*-4,7-methanoindene-*cis,cis*-1,3-dicarboxylate. Precursor to 34.** Aldrin was converted to its dihydro derivative[80] which was then reduced to the known perhydrodimethanonaphthalene, bp 62–65° at 0.75 Torr (lit.[78] bp 105 at 22 Torr). The oxidative procedure described for the exo,endo isomer yielded the dicarboxylic acid, mp 224–227°. Esterification gave the diester mp 91–94° which gave only one peak in glpc (3% SE-30 at 162°): pmr ($CCl_4$) δ 1.33 (broad s, 6), 2.1–2.45 (m, 4), 2.50–2.65 (m, 4), 3.66 (2, 6); mass spectrum (16 eV) *m/e* (rel intensity) 252 (1), 221 (50), 190 (75); high resolution (MS-902) mass of parent ion 252.1367 (calcd for $C_{14}H_{20}O_4$, 252.1361).

**5,6-Dichloro-7-isopropylidenebicyclo[2.2.1]-2-heptene-5,6-dicarboxylic Anhydride. Precursor to 41.** 7,7-Dimethylfulvene and dichloromaleic anhydride in chloroform reacted over a period of 3 days. The brown crystals obtained upon evaporation of the chloroform were purified by chromatography on silica gel with hexane–chloroform elution to give material: mp 86–89°; pmr ($CDCl_3$) δ 1.62 (s, 6), 4.08 (m, 2), 6.65 (m, 2).

***endo,cis*-2-Hydroxy-3-*tert*-butyldimethylsiloxybicyclo[2.2.1]-hept-5-ene.** *endo,cis*-Bicyclo[2.2.1]hept-5-en-2,3-diol[81] (2.86 g, 22.6 mmol), *tert*-butyldimethylchlorosilane (4.26 g, 27.1 mmol), and 3.84 g (56.5 mmol) of imidazole were added to 25 ml of THF.[82] After 5 hr at 25° the diol could no longer be detected by tlc and the reaction mixture was treated with 60 ml of water and then extracted with 3 × 50 ml of methylene chloride. The methylene chloride solution was washed with water, dried ($MgSO_4$) and evaporated at 25° to give a residue which was chromatographed on 330 g of silica gel using benzene (84%)–ethyl acetate (16%) eluent to give 3.85 g (72%) of the desired product: bp 60–69° (0.13 Torr); pmr ($CDCl_3$) δ 6.1 (nearly collapsed AB quartet, 2), 4.1 (m, 2), 2.9 (m and d, 3, *J* = 6.5 Hz, d disappeared with $D_2O$), 1.4 (d of t, 1, *J* = 10 Hz), 1.1 (d, 1, *J* = 10 Hz), 0.9 (s, 9), 0.14 (s, 6).[63]

***endo*-3-*tert*-Butyldimethylsiloxybicyclo[2.2.1]hept-5-en-2-one. Precursor to 35.** Oxidation of 3.4 g of the alcohol was accomplished by use of 8 mmol of $CrO_3$ and 16 mmol of pyridine in 20 ml of methylene chloride under anhydrous conditions. After reacting for 20 min the methylene chloride solution was filtered, washed with 10 ml of 7% aqueous $NaHCO_3$, 10 ml of water, and 10 ml of saturated aqueous NaCl, and dried over $MgSO_4$. The solvent was removed under vacuum and residue was dissolved in ether, filtered, and, after vacuum evaporation of the ether, purified by chromatography on 205 g of silica gel using benzene as the eluent to give after distillation the ketone in a 57% yield: pmr ($CDCl_3$) δ 6.5 (d of d, 1, *J* = 5 and 3 Hz), 6.1 (m, 1), 4 (d, 1, *J* = 4 Hz), 3.1 (m, 2), 2.3 (d of t, 1, *J* = 2 and 10 Hz) 1.9 (d, 1, *J* = 10 Hz), 1.0 (s, 9), 0.2 (s, 6).[63]

***exo*- and *endo*-7-Isopropylidenebicyclo[2.2.1]hept-5-ene-2,3-diol Carbonate.**[83] Vinylene carbonate (6.4 g, 0.075 mol) and 6,6-dimethylfulvene (5.3 g, 0.05 mol) in 23 g of toluene were heated for 5 hr at 150° and after cooling evaporated at 35° at 1 Torr. The resulting viscous oil was chromatographed on 380 g of silica gel (benzene eluent) to give 1.2 g (12%) of nearly pure endo isomer and a mixture of endo and exo isomers. Crystallization from $CCl_4$ gave 1.3 g (14%) of pure exo isomer, mp 70–72° (lit.[83] 74–76°), and 2.9 g (30%) of a mixture of the isomers.

***exo*- and *endo,cis*-3-*tert*-Butyldimethylsiloxy-7-isopropylidenebicyclo[2.2.1]hept-5-en-2-ol.** The mixture of exo and endo carbonates (4.1 g) was hydrolyzed by rapidly stirring the carbonates dissolved in 40 ml of ether with 4.1 g of KOH in 40 ml of water for 2 hr at 25° to yield 3.1 g (86%) of a crystalline mixture of exo and endo diols. The diols were converted to the *tert*-butyldimethylsiloxy ether by use of 1.1 equiv of the silyl chloride[81] to give after chromatography on silica gel (hexane (94%)–ether (6%) eluent) and distillation 1.61 g (31%) of material bp 85–97° (0.09 Torr).[63]

***endo*-3-*tert*-Butyldimethylsiloxy-7-isopropylidenebicyclo-[2.2.1]- hept-5-en-2-one. Precursor to 42.** Oxidation of the mixture of *exo*- and *endo*-hydroxy *tert*-butyldimethylsiloxy ethers (1.6 g) with $CrO_3 \cdot 2Py$ in methylene chloride gave a crude product which was chromatographed on 110 g of silica gel [hexane (95%)–ethyl acetate (5%) eluent] to give the crude ketones from which 0.51 g (32%) of the desired endo derivative, bp 85–92° at 0.13 Torr, could be separated by glpc on a 6 ft 0.75 in. 7% Carbowax 6000 column at 140°: pmr ($CDCl_3$) $\delta$ 6.6 (d of d, 1 $J$ = 5.1 and 2.5 Hz), 6.3 (m, 1), 4.0 (d, 1, $J$ = 3.5 Hz), 3.7 (m, 2), 1.81 and 1.76 (singlets, 6), 1.07 (s, 9), 0.29 (s, 6).[63]

Mixing the siloxy ketone (0.05 $M$) in DMSO with 0.10 $M$ potassium *tert*-butoxide in DMSO gave the rearranged semidione **42** at a maximum concentration about 50 sec after mixing in a flow cell having a lag volume of 0.10 ml.

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## References and Notes

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