Aliphatic Semidiones. XXIX. Cycloheptane-1,2-semidione[1,2]

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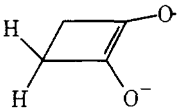
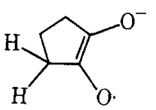
Abstract: An analysis of long-range esr hyperfine splittings for a series of cycloheptane-1,2-semidiones allows the chair conformation to be assigned. Extended Hückel calculations support the experimental hfs assignments. Numerous rigid bi- and tricyclic derivatives of cycloheptanesemidione showing long-range splittings in their esr spectra are described particularly in the bicyclo[3.2.1]octane-6,7-semidione, bicyclo[3.2.2]nonane-6,7-semidione, bicyclo[3.3.2]decane-9,10-semidione, and bicyclo[4.2.1]nonane-3,4-semidione series. The possible conformations of bicyclo[4.1.0]heptane-3,4-semidione, bicyclo[3.2.0]heptane-6,7-semidione, and bicyclo[3.2.0]heptane-2,3-semidione are considered, and conformational assignments are made for bicyclo[4.2.1]nonane-3,4-semidione, bicyclo[3.2.2]nonane-6,7-semidione, and bicyclo[3.3.2]decane-10,11-semidione, all of which possess the cycloheptene ring in a boat conformation. Bicyclo[3.2.2]nonane-2,3-semidione appears to have a symmetrical conformation. The relative magnitudes of nonbonded interactions in bicyclic semidiones are discussed and compared.

In previous papers, we have considered the esr hyperfine splitting constants (hfsc) and geometry of cyclobutane (**1**),[4] cyclopentane (**2**),[5] and cyclohexane (**3**) semidiones.[6] It has been argued that the cycloalkanesemidiones are reasonable conformational models for the cycloalkenes.[6] Following this reasoning, we have made a thorough study of cycloheptanesemidione including numerous bi- and tricyclic derivatives where the cycloheptene ring is held rigidly in a chair or boat structure.



1

(a_{α}^{H} = 13.9 G (4), DMSO)



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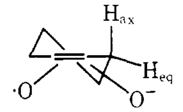
(a_{α}^{H} = 13.1 G (4), DMSO)



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(a_{ax}^{H} = 13.10 G (2); a_{eq}^{H} = 6.55 G (2); θ_{ax}^{H} = 14°; θ_{eq}^{H} = 134°; $\Delta H^{\ddagger}$(ring inversion) = 4 kcal/mol

Reasonable conformations for cycloheptene are the chair (**4**), boat (**5**), or twist (**6**) structures.[7] Calculations[8,9] have indicated a slight thermodynamic preference for the boat form of cycloheptene, whereas the nmr spectrum of 5,5-difluorocycloheptene has been interpreted in terms of a chair structure with ΔH^* for ring inversion = 7.4 kcal/mol.[10] A chair structure (>92%) is also indicated by the dipole moment of 1,2-benzocyclohepten-5-one[11] and the nmr spectrum of 4,4,6,6-tetradeuterio-1,2-benzocycloheptene (>95%),[12] whereas for 3,3,6,6-tetramethyl-1,2-benzocycloheptene[13] and a variety of 1,3-dithiapenes, 1,3-dioxapenes, and their benzo derivatives,[14,15] a mixture of conformations has been detected by nmr spectroscopy.

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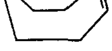

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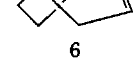

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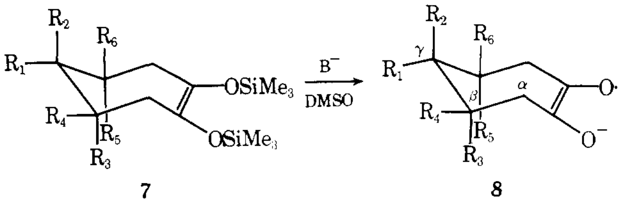
We have previously reported[6] that cycloheptanesemidione possesses a single rigid conformation at 25° in esr spectroscopy with resolved hfsc of 0.26 G. This means that ΔF^* for ring inversion must be >6.5 kcal/mol, in reasonable agreement with the nmr result.[10] Our initial goal in the present work was to distinguish the preferred conformation of cycloheptanesemidione. After having eliminated **5** and **6** as possible conformations for the parent monocyclic semidione, we have attempted to define the uniqueness of long range hfsc in bicyclic semidiones containing the partial structures **4** and **5**. Finally, we attempt to apply the results to conformational analysis of various bicyclic semidiones where flexibility exists.

Results

Cycloheptanesemidione. Acyloin condensation of diethyl pimelate in the presence of trimethylchlorosilane produced bis(trimethylsiloxy)cycloheptene **7a** which in dimethyl sulfoxide (DMSO) containing potassium *tert*-butoxide gave a strong esr signal for the semidione[16] **8a** yielding at −10° a well resolved spectrum with hfs by nine hydrogen atoms (Scheme I). In DMSO-d_6 the hfs of the hydrogen atoms α to the semidione spin label were replaced by deuterium atoms **8b**.[17] The only set of consistent hfsc are assigned in Table I.

Scheme I



7 **8**

a, R_1-R_6 = H
b, R_1-R_6 = H, α-D (4)
c, R_1 = CH_3; R_2-R_6 = H
d, R_1 = R_2 = CH_3; R_3-R_6 = H
e, R_4 = CH_3; R_1-R_3, R_5, R_6 = H
f, R_4 = CH_3; R_1-R_3, R_5, R_6 = H, α-D (4)
g, R_4 = R_6 = CH_3; R_1-R_3, R_5 = H
h, R_4 = R_5 = CH_3; R_1-R_3, R_6 = H
i, R_4 = R_5 = CH_3; R_1-R_3, R_6 = H, α-D (4)
j, R_1 = R_3 = D; R_2, R_4-R_6 = H
k, R_2 = R_4 = D; R_1, R_3, R_5, R_6 = H

The twist or twist-boat conformation (**6**) is immediately eliminated from consideration for the semidione, because it would require two equivalent γ-hydrogen atoms in **8a**, **8b**, and **8e–f**. Moreover, the twist-boat with *cis*-β,β′-dimethyl

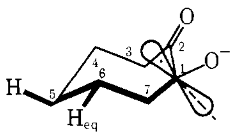
Table I. Assignment of Hfsc in **8a–i**

	a^H, G				
Struct	α-Axial	α-Eq	β-Eq	β-Axial	γ-Eq
8a	6.60 (2)	0.28 (2)	2.05 (2)	0.28 (2)	0.54 (1)
8b	1.00 (2)[a]	*b*	2.05 (2)	0.28 (2)	0.54 (1)
8c	6.62 (2)	0.29 (2)	1.88 (2)	0.29 (2)	
8d	6.90 (2)	0.29 (2)	1.85 (2)	0.29 (2)	
8e	6.60 (2)	0.32 (2)	2.15 (1)	0.32 (2)	0.3–0.4 (1)
8f	1.00 (2)[a]	*b*	2.15 (1)	0.28 (2)	0.40 (1)
8g	6.50 (2)	0.32 (2)		0.32 (2)	0.32 (1)
8h	6.81, 7.25	0.33 (2)	0.66 (1)	0.33 (1)	0.33 (1)
8i	1.05 (2)[a]	*b*	0.66 (1)	0.33 (1)	0.33 (1)

[a] a^D. [b] Not observed.

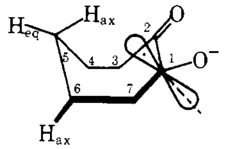
(**8g**) or *trans*-β,β'-dimethyl (**8h–i**) substituents would require symmetries in the reverse of those observed (*i.e.*, two different a_β^H in **8g**, two equivalent a_β^H in **8h–i**).

Only a single isomer was observed for **8c** and **8e–g**. This is consistent with either a chair or a boat conformation in which the methyl groups have taken the preferred equatorial positions. We notice that the long-range hfs at the γ position is by the equatorial hydrogen atom. However, this result can be rationalized with either the boat or chair conformation. Substitution of β-methyl groups in the equatorial position (**8e–i**) replaces the hydrogen atoms with $a^H \sim 2$ G, and this is consistent only with the chair structure. The long-range hfs which follows a zig-zag coplanar arrangement of bonds and orbitals[17,18] predicts that at the β position $a_{eq}^H/a_{ax}^H \gg 1$ for the chair conformation and $\ll 1$ for the boat conformation (**9**, **10**). This assignment is fully confirmed by EH-SCF calculations and by experimental hfsc for rigid polycyclic semidiones to be discussed in the following sections.



9

(2-V and 2.5-V long-range interaction shown)



10

(expected 2-V long-range interaction shown)

By simultaneous solutions of the Heller–McConnell equations[19,20] for the α-hydrogen atoms in cycloheptanesemidione, one obtains:

$$a_{ax}^H = 6.60\text{ G} = \rho_C\beta\cos^2\theta_{ax} \tag{1}$$

$$a_{eq}^H = 0.32\text{ G} = \rho_C\beta\cos^2\theta_{eq} \tag{2}$$

Simultaneous solution with $\theta_{eq} = \theta_{ax} + 120°$ gives two possible solutions, $\theta_{ax} = -19°$, $\rho_C\beta = 7.5$ G and $\theta_{ax} = -39°$, $\rho_C\beta = 11.1$ G. For cyclopentanes and cyclohexanesemidiones, $\rho_C\beta$ is 17.6 and 14.0 G.[20] It would appear that the solution with $\theta_{ax} = -39°$ (the axial hydrogen atom pointing inside the ring) yields the most reasonable value of $\rho_C\beta$ even though nmr measurements of cycloheptene itself have yielded a value of $\theta_{ax} = -19°$ for the α-hydrogen atom.[21] The lack of consistency in $\rho_C\beta$ for the C_5, C_6, and C_7 monocyclic semidiones is thought to reflect the absence of terms for the second dihedral angles (φ_{ax} and φ_{eq}) in the Heller–McConnell equation (Figure 1) since it is unreasonable that ρ_C would vary by 30–50% between cyclopentane and cycloheptanesemidiones.

We have previously described a highly successful EH-SCF method of calculating hfsc for semidiones using the geometry of structure **11**.[22-24] We have applied this technique to structures **9** and **10** with all d(C–C) = 1.54 Å and d(C–H) = 1.09 Å and with the β- and γ-hydrogen atoms so located that ∠HCH = 120°, and all CCH angles were

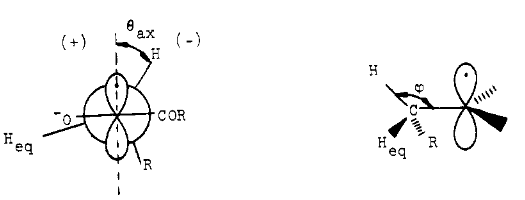
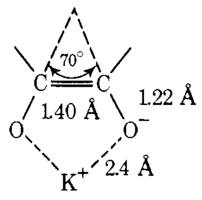


Figure 1. Definition of φ and θ for hydrogen atoms adjacent (α) to a spin label.



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equivalent for a given group. Calculations were performed with three reasonable geometries (structures A, B, C) varying mainly in the values of $\theta_{\alpha\text{-H}}$. Results of the calculations are given in Table II. (Structure A: $\theta_{ax} = -11°$, $\theta_{eq} = 71°$ (or 109°); ∠C(2)C(3)C(4) = ∠C(3)C(4)C(5) = ∠C(4)C(5)C(6) = 109°. Structure B: $\theta_{ax} = -19°$, $\theta_{eq} = 79°$ (or 101°); ∠C(2)C(3)C(4) = ∠C(3)C(4)C(5) = 111°, ∠(4)C(5)C(6) = 107°. Structure C: $\theta_{ax} = -39°$, $\theta_{eq} = 81°$; ∠C(2)C(3)C(4) = ∠C(3)C(4)C(5) = 111°; ∠C(4)C(5)C(6) = 110°.)

With all the geometries employed, the chair conformation **9** was in better agreement with the experimental results than the corresponding boat structure (**10**). However, it would be unwise to make a choice between structures **9A**, **9B**, or **9C** on the basis of the calculations performed because of the various inadequacies in the geometries employed and in view of the multitude of further minor geometric modifications possible.

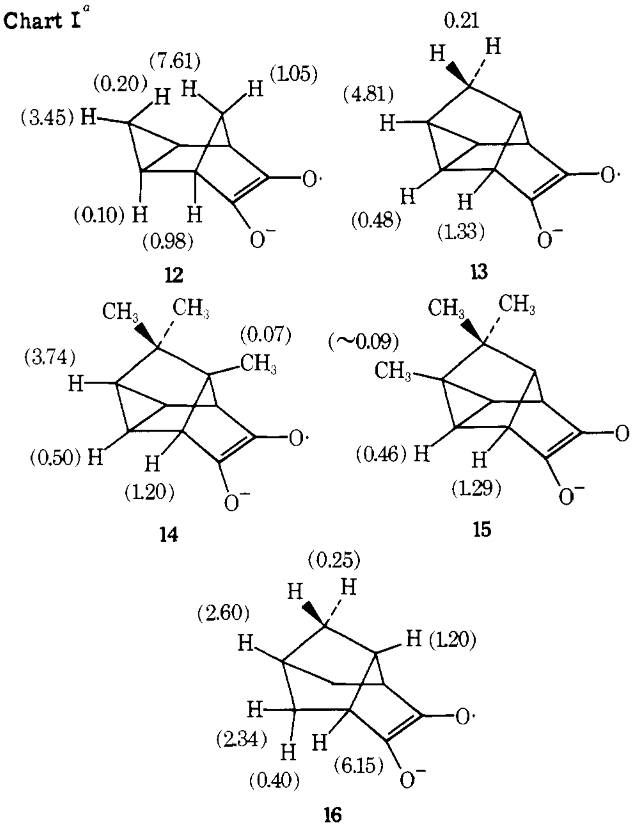
Semidiones Containing a Rigid C_7 Chair Structure. A number of bicyclic and tricyclic derivatives of **9** have been prepared in the bicyclo[3.2.1]octane-6,7-semidione (**12–15**), bicyclo[3.2.2]nonane-6,7-semidione (**16**), bicyclo[3.3.2]decane-9,10-semidione (**17–19**), and bicyclo[4.2.1]nonane-3,4-semidione (**20–23**) families.

Semidiones **12–16** provide further examples of 2-V and 2.5-V long range interactions by equatorial hydrogen atoms at the β and γ positions in the basic skeleton of **9**. There is no problem in assigning a consistent set of hfsc to **12–16** (Chart I). The long range splittings in **12–15** have been discussed previously as representatives of bicyclo[2.2.1]heptanesemidiones.[24] Moreover, the EH-SCF calculation for **12** is in excellent agreement with observed value of hfsc, particularly in regard to the large value for the anti hydrogen at C-3 (~3 G), Table II.[24] Semidione **13** displays the largest 2.5-V long-range splitting[25] yet observed for a semidione.

Further examples of the long range 2.5-V interaction by the equatorial γ-hydrogen atom are found in semidiones **17–20** which contain the bicyclo[3.2.2]nonane or bicyclo[3.3.2]decane ring systems (Chart II). In **17–19**, the bridgehead hydrogen at C-1 and C-5 are in or near the nodal plane of the π system, and a^H is either not observed or is very small.[26] EH-SCF calculations for **17** are given in Table II. The calculation predicts a lower value of a_α^H for **17** than for **12** as well as the highly stereospecific nature of the hfs by γ-hydrogen atoms in both **12** and **17**.

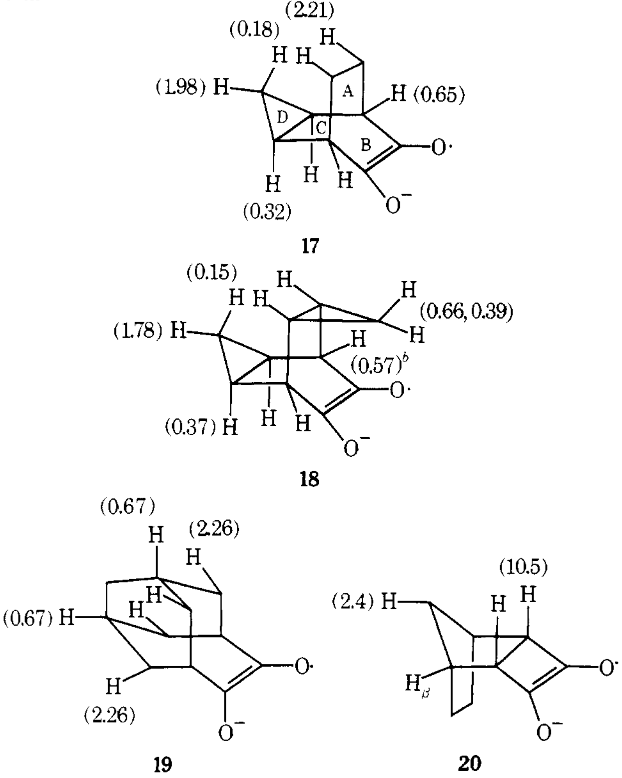
In structures **20** and **21** are summarized the hfsc for some previously reported cyclobutanesemidiones[4] which contain a seven-membered ring as part of a bicyclo[4.2.1]nonane system. Closing the four-membered ring has distorted the

Chart I[a]



[a] a^H in G.

Chart II[a]

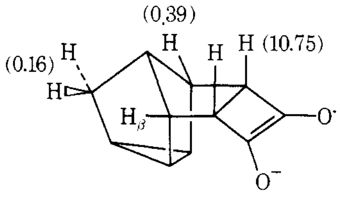


[a] H in G. [b] Proved by deuterium substitution.

Table II. EH-SCF Calculations of Hyperfine Splitting Constants for Cycloheptane Semidiones

	a^H, G					
	α		β		γ	
Structure	Ax	Eq	Ax	Eq	Ax	Eq
9A	7.26	0.93	0.24	2.15	0.29	1.37
9B	8.21	0.43	0.27	1.90	0.12	1.26
9C	6.15	0.60	0.83	1.24	0.00	1.90
8, exptl	6.6	0.3	0.3	2.1	0	0.6
10A	7.33	2.09	1.97	0.01	4.20	5.07
10B	9.56	1.10	1.24	0.17	2.21	2.47
10C	9.18	0.25	0.22	0.09	1.51	0.92
12, exptl		0.98	0.10		0.20	3.5
12, calcd[a,b]		1.04	0.03		0.35	2.97
17, exptl[c]		0.65	0.3		0.2	2.0
17, calcd[a,c]		0.13	0.00		0.10	2.06
25, exptl[d]		2.9	0.3		0.15	0.5
25, calcd[d,e]		2.25	0.48		0.56	0.74
26, exptl[f]		0	0.2		0.4	0.5
26, calcd[e,f]		0.03	0.34		0.86	1.26

[a] Geometry (*d*), Table III, ref 24. [b] a_{8a}^H = 7.61, a_{8s}^H = 1.05; calcd 7.54, 0.85 G. [c] $a_{8,9a}^H$ = 2.2, $a_{8,9s}^H$ = 0; calcd 1.60, 0.47 G. [d] a_{8a}^H = 7.78, a_{8a}^H = 1.37; calcd 8.06, 1.06 G. [e] Angle between planes A, B, C = 120°, between planes C, D = 115°, *d*(C-1–C-5) = 2.65 Å. [f] $a_{8,9a}^H$ = 2.3, $a_{8,9s}^H$ = 0.1; calcd 2.00, 0.50 G.



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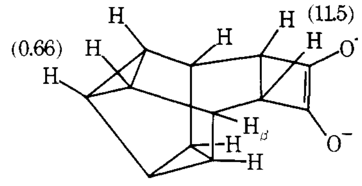

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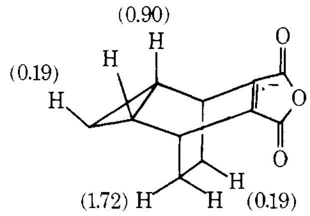
(a^H = 0.38 (6) G, H_β and H_γ)

chair conformation considerably and caused the β (equatorial) hydrogen to assume a position nearly in the nodal surface of the MO occupied by the unpaired spin. The value of $a_{\beta\text{-eq}}^H$ decreases from 2.1 in **9** to ~0.4 in **21** and its derivatives. The staggered nine-membered ring of **22** also has a_β^H ~ 0.4 G. In **20**, the 2.5-V interaction with one γ-hydrogen atom is observed, while in **21** and **22**, a 3-V interaction is seen. The mechanism of the 2.5-V interaction of H_γ in **8**, **12–14**, and **16–20** was investigated by changing the symmetry of the HOMO of the spin label. The semifuraquinone **23** was synthesized by electrolysis of the dichloro derivative in DMSO. Although in **12–19** $a_\gamma^H \gg a_\beta^H$, in **23** a_β^H = 0.90 G $\gg a_\gamma^H$ = 0.19 G. This difference reflects the difference between a spin polarization mechanism (**23**) and a delocalization mechanism (**12–19**). Another example of long-range hfs similar to H_γ in **23** has been reported[27] for **24** where H_γ in the conformation shown lies in the nodal plane of the spin label.



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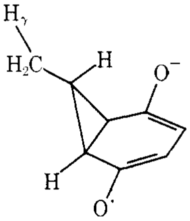

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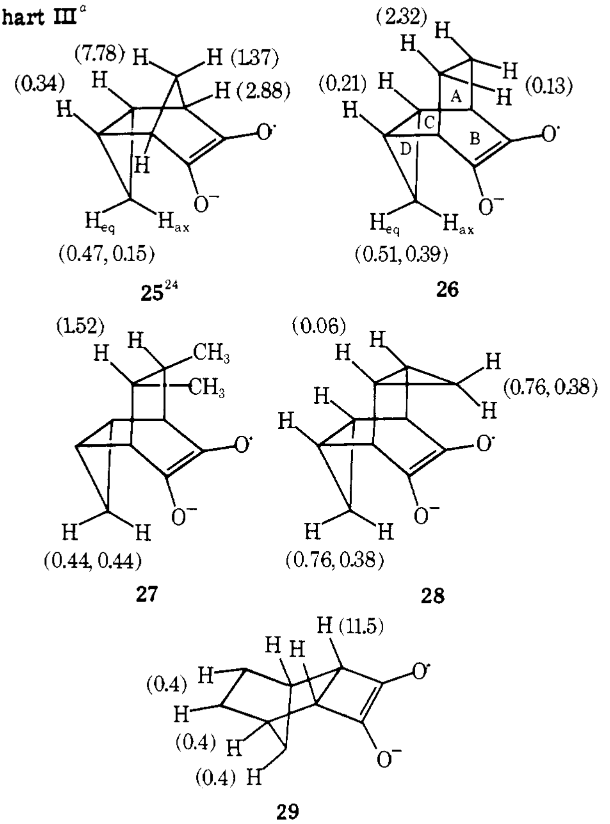
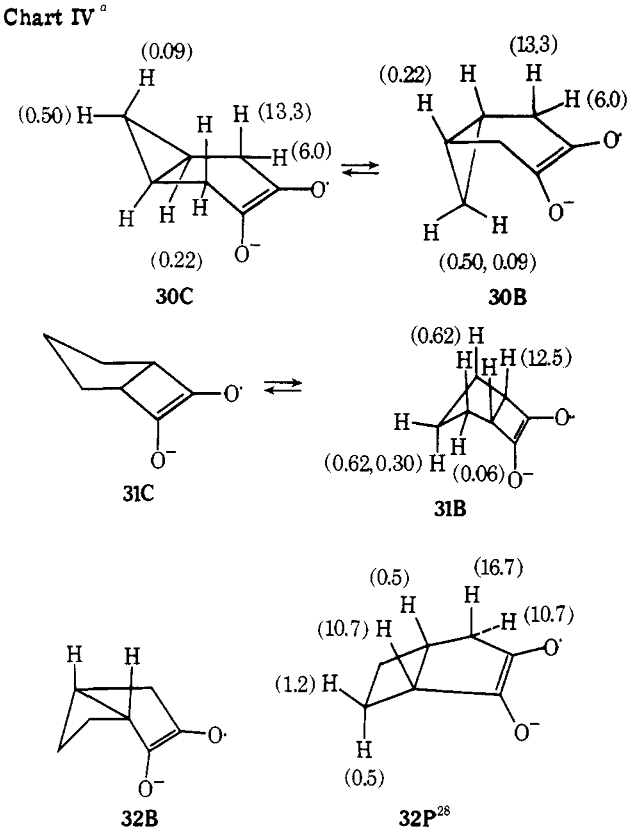
Semidiones Containing a Rigid C_7 Boat Structure. In Chart III are listed bi- and tricyclic semidiones in the bicyclo[3.2.1]octane, bicyclo[3.2.2]nonane, bicyclo[3.3.2]decane, and bicyclo[4.2.1]nonane series which contain a cycloheptene ring locked into the boat conformation.

Chart III[a]



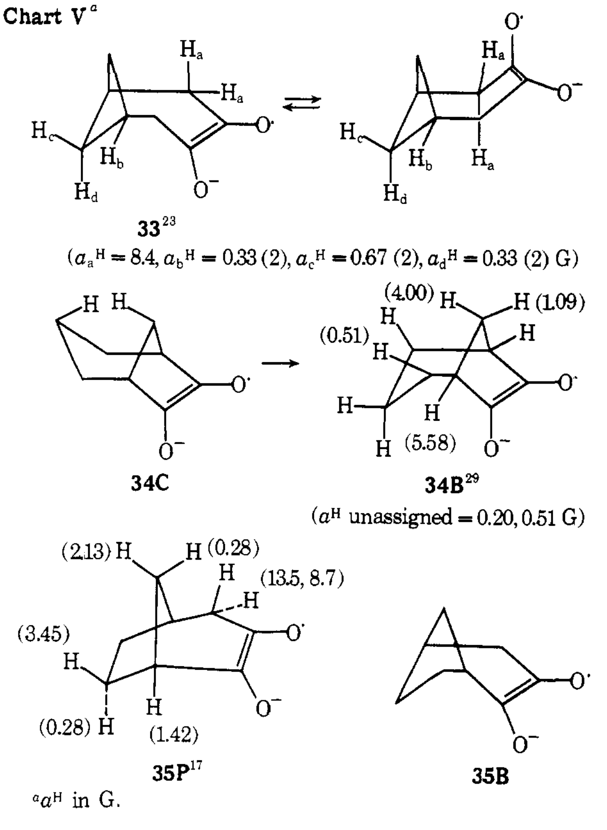
[a] a^H in G.

Chart IV[a]



[a] a^H in G.

Chart V[a]



[a] a^H in G.

EH-SCF calculations for **25** have been reported previously[24] and are summarized in Table II together with a calculation for **26**. These calculations correctly predict the variation in $a_\alpha{}^H$ (from 2.9 G in **25** to 0 in **26**), the low value of $a_\beta{}^H$ (~0.2–0.3), and the near equivalence of the two γ-hydrogen atoms in both **25** and **26**.

Nonrigid Bicyclic Semidiones Containing a C_7 Ring. The previous sections have established that a chair conformation for cycloheptanesemidione will have a large hfs by equatorial hydrogen atoms at C(β) and C(γ), whereas the boat structure will have hfs by axial and equatorial β- and γ-hydrogen atoms of roughly the same magnitude. We examined cycloheptanesemidione bridged between C(4)–C(6), C(3)–C(7), and C(3)–C(6) by a zero, one, two, and three carbon bridge. Chart IV lists the three bicyclic semidiones containing a zero carbon bridge. Bicyclo[4.1.0]heptane-3,4-semidione (**30**) has hfsc most reasonably assigned to the chair-type structure (**30C**). However, the values of $a_\alpha{}^H$ indicate that the conformation must be highly distorted from that of **9**. Bicyclo[3.2.0]heptane-6,7-semidione[4] seems to be boat-like (**31B**) based on the values observed for $a_\gamma{}^H$. Calculations (EH-SCF) for **31** using a geometry of two planes with an angle of intersection = 115–120° also gave reasonable agreement with the observed hfsc.[4] Semidione **32B** was prepared from precursors with a cis-ring juncture which was undoubtedly maintained in the semidione.[28] This forces the molecule to assume a boat-like structure (**32B**) or a conformation where both the cyclobutane and cyclopentene rings are essentially planar (**32P**). Although conformational motion is possible for **30–32**, none was detected by variable temperature esr studies.

The three isomeric semidiones of Chart V involve a methano bridge between C(4)–C(6) (**33**),[23] C(3)–C(7) (**34**),[17,29] and C(3)–C(6) (**35**)[17] of the cycloheptene ring.

In **33**, rapid conformational motion is observed even at −80°.[23] Semidione **34** undoubtedly exists with the seven-membered ring in a boat conformation. The observed hfsc are consistent with this interpretation. For example, by analogy with structures **12–16**, a value of $a_\gamma{}^H$ for structure **34C** of 2.5–5 G would be expected. Semidione **35** gives a rich long range hfs pattern proved by alkyl and deuterium substitution.[17] There seems to be no evidence that the seven-membered ring is still in a boat-like conformation; a

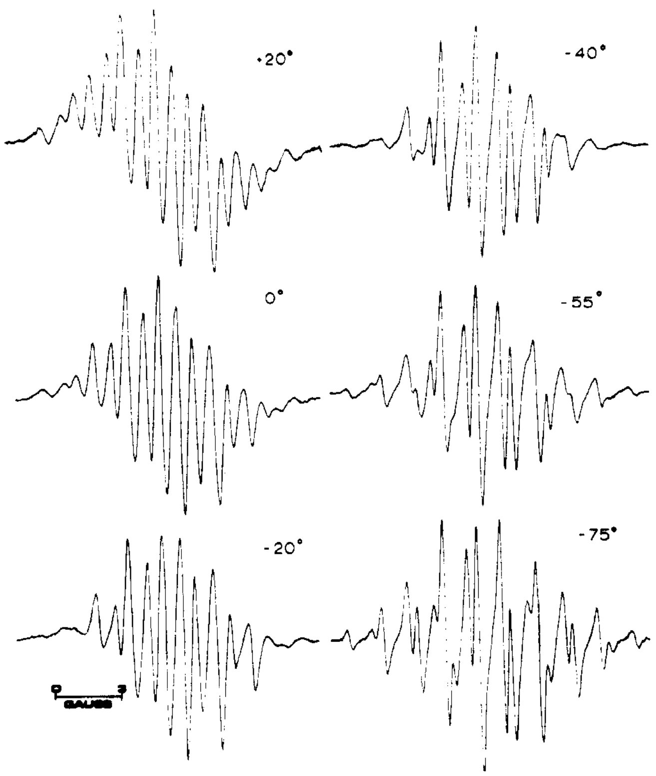


Figure 2. First derivative esr spectra of **37a** in DMF (80%)-DMSO (20%), potassium gegenion.

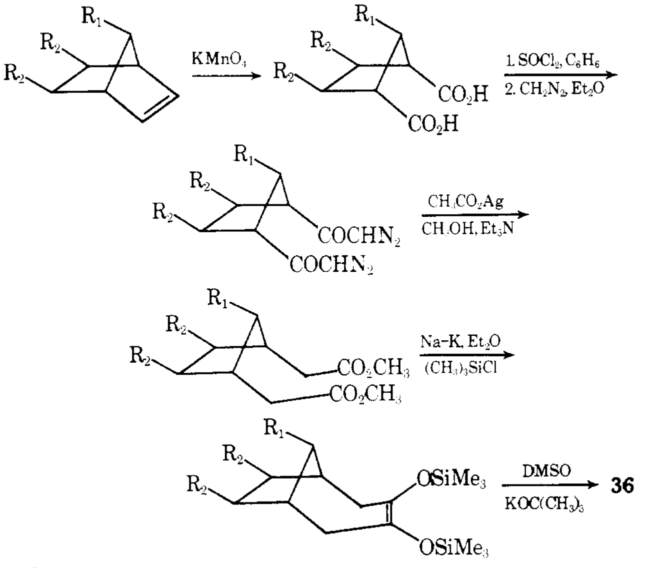
conformation wherein C(1)-C(5) is one plane, and C (1), C(5)-C(7) in another plane is preferred, *e.g.*, **35P**.

A two-carbon bridge in the cycloheptene system leads to the semidiones of Chart VI.

Semidiones **36a,b,c** were synthesized by Scheme II. By analogy with **20** and **29**, the boat-like conformation for **36B** seems definitely to be preferred with $a_{9\text{-anti}}{}^{H} = a_{7,8\text{-anti}}{}^{H}$ = 0.53, 0.56, $a_{2,5\text{-axial}}{}^{H}$ = 9.85, $a_{2,5\text{-eq}}{}^{H}$ = 1.56, and $a_{1,6}{}^{H}$ = 0.25 G.

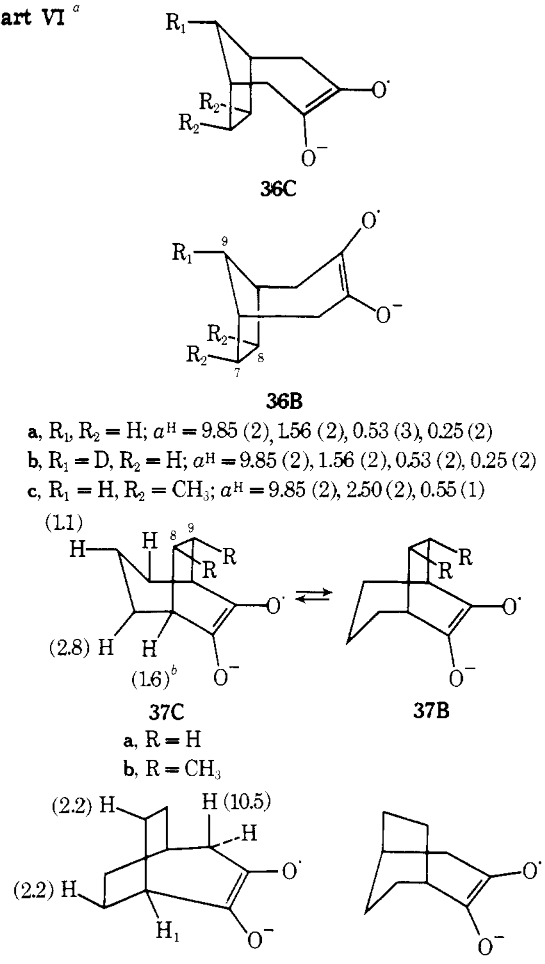
Semidiones **37a,b** were prepared from the appropriate olefins *via* the oxidation, chain extension, and acyloin condensation route described in Scheme II. The synthesis of the appropriate bicyclo[3.2.2]nonenes is shown in Scheme III. The esr spectra for **37a** and **37b** showed temperature dependence suggesting the interconversion of conformers **37C** and **37B** (Figure 2). At −75° for **37a**, the spectrum is consistent with conformation **37C** with $a_{8,9\text{-anti}}{}^{H}$ = 1.55, $a_{1,5}{}^{H}$ = 1.55, $a_{2,4\text{-eq}}{}^{H}$ = 2.75, and $a_{3\text{-eq}}{}^{H}$ = 1.12 G. At +100°, time averaging of conformation **37C** and **37B** gives a spectrum with a^{H} = 1.95 (2), 1.55 (2), 1.40 (2), and 0.80 (1) G. In a similar fashion **37b** gives at −85° a spectrum consistent with the chair-like conformation with $a_{8,9\text{-anti}}{}^{H} = a_{3\text{-eq}}{}^{H}$ = 0.9, $a_{2,4\text{-eq}}{}^{H}$ = 2.8, $a_{1,5}{}^{H}$ = 1.6 G. At +20°, the spectrum shows a^{H} = 1.6 (4), 0.8 (3), and 0.1 (6) G.

Scheme II[a]



[a] $R_1 = R_2 = H$; $R_1 = D, R_2 = H$; $R_1 = H, R_2 = CH_3$.

Chart VI[a]



36C

36B

a, $R_1, R_2 = H$; a^H = 9.85 (2), 1.56 (2), 0.53 (3), 0.25 (2)
b, $R_1 = D, R_2 = H$; a^H = 9.85 (2), 1.56 (2), 0.53 (2), 0.25 (2)
c, $R_1 = H, R_2 = CH_3$; a^H = 9.85 (2), 2.50 (2), 0.55 (1)

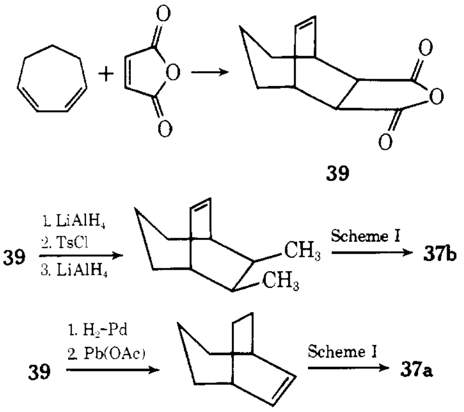
37C **37B**
a, R = H
b, R = CH_3

38P[17] **38B**

[a] a_H in G. [b] Proven by deuterium substitution.

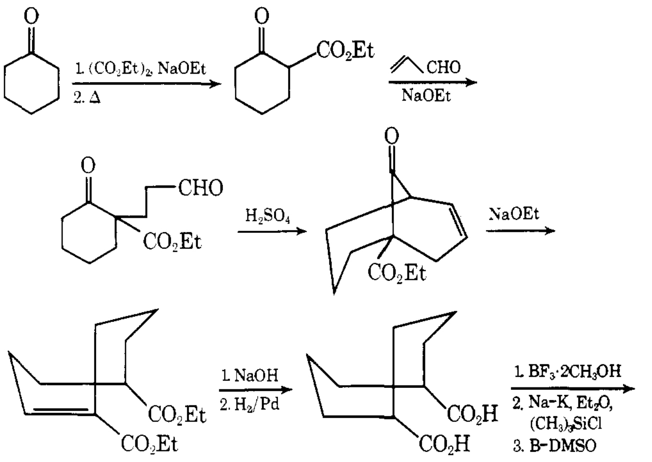
Semidione **38** gives no evidence of conformational motion or possessing a dissymetric conformation.[17] The value $a_1{}^{H}$ is zero indicating this hydrogen atom is in the nodal plane. Conformation **38P** is preferred.

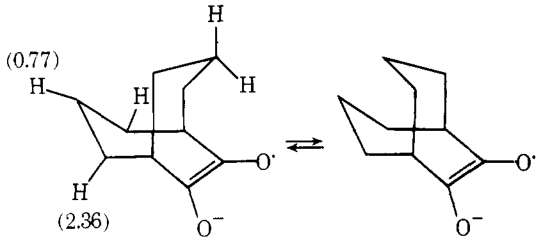
Scheme III



The cycloheptene derivative with a trimethylene bridge between C(3) and C(7) in the cycloheptene ring was synthesized according to Scheme IV.

Scheme IV





40C, B **40C, C**

The spectrum of **40** at +25° was difficult to interpret and may involve a mixture of conformations. However at −80°, the spectrum seems to be clearly that expected for **40C,B** with a^H = 2.36 (2), 0.77 (1), and 0.42 (1) G (see ref 2 for the experimental spectra). The hfs of 2.36 and 0.77 G are assigned to the β- and γ-equatorial hydrogen atoms in the chair-like ring and the 0.42-G hfs to one of the γ-hydrogen atoms in the boat-like ring.[2]

Discussion

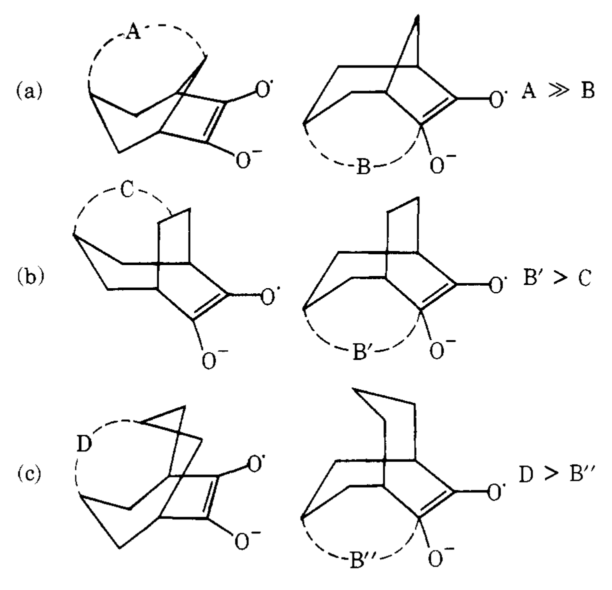
The conclusions from the previous section allows a series of nonbonding interactions to be qualitatively compared, Chart VII.

The semidione spin label appears to be a good model for an olefin. Thus the bis(trimethylsilyl) ether of bicyclo[3.3.2]dec-9-ene-9,10-diol exists in the chair-boat conformation[30] as does the semidione **40** and the quinoxaline derivative of bicyclo[3.3.2]decane-9,10-dione.[31] Replacement of the ethylene bridge by the methylene bridge[32] or ethano bridge[30,33] in the tricyclo[3.3.*n*] system leads to a preferred twin chair conformation in which there is either considerable flattening of the rings[32] or twisting of the rings[30] to relieve interaction D (Chart VII) between inside substituents at C-3 and C-7.[34]

Experimental Section

Preparation of Semidiones. The semidiones were usually prepared from the appropriate diester by reaction of a 10–50-mg sample of the pure diester and 1–2 ml of trimethylchlorosilane in diethyl ether or dimethoxyethane for 5 min with 0.1–0.2 ml of sodium-potassium alloy (1:3) with vigorous stirring under a nitrogen atmosphere for 1–4 hr before filtration.[16] The filtrate was evaporated under vacuum leaving as an oil or solid the bis(trimethylsiloxy)alkene which could be converted to the semidione by treatment with an excess of potassium *tert*-butoxide in DMSO under a nitrogen atmosphere using an inverted mixing cell described previously.[35] Spectra were recorded with either a Varian Associates E-3 or V-4500 spectrometer with 100-KHz field modulation and 4- or 9-in. magnets, respectively.

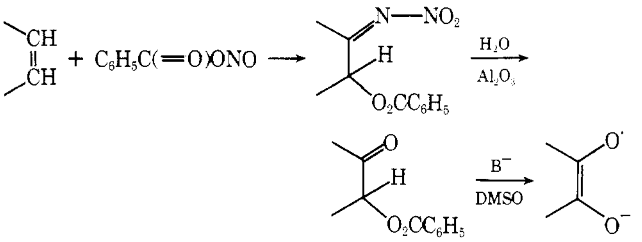
Chart VII



One general route to the desired dibasic esters involved oxidation of the appropriate cyclic or bicyclic olefin by potassium permanganate followed by esterification using diazomethane, methanol, and acid, or the boron trifluoride-methanol complex.[36] In a typical oxidation, the potassium permanganate was added dropwise to the olefin dissolved in acetone at 0° over a 6-hr period. After warming to 25°, the solution was stirred an additional 10 hr before filtration. The filter cake containing the potassium salt of the diacid was stirred in water and the manganese dioxide reduced by sulfur dioxide after which the solution was acidified to Congo Red with sulfuric acid and extracted three times with 100 ml of ether. The combined ether extracts were reduced to 50 ml volume and extracted three times with 20 ml of 10% aqueous sodium bicarbonate. These extracts were acidified to Congo Red and extracted three times with 100 ml of ethyl acetate. Removal of the ethyl acetate under vacuum left the crude diacid which after esterification in methanol solution was purified by glpc.

An alternate route to the semidione from 1,2-disubstituted mono olefins involved the addition of benzoyl nitrite[37] in methylene chloride solution in an nmr tube. After the olefinic absorption had disappeared, the mixture was added to 10 ml of methylene chloride and washed with 10% aqueous sodium bicarbonate. After distillation of the solvent under reduced pressure, 25 ml of hexane (75%)-benzene (25%) was added along with 3 g of grade III alumina, and the resulting mixture was refluxed for 4 hr. The mixture was dried ($MgSO_4$) and filtered, and the solvent was evaporated to give the benzoic acid ester of the α-hydroxy ketone (Scheme V) which was added to deoxygenated DMSO containing potassium *tert*-butoxide without further purification.

Scheme V



Synthesis of Dimethyl Pimelates. Precursors to 8a–k. Dimethyl 4-methylpimelate was prepared from the corresponding glutaric acid *via* the Arndt–Eistert reaction sequence. The following general procedure was used for all chain extensions of this type. 3-Methylglutaric acid (3.8 g, Aldrich Chemical Co.) was added to 40 ml of benzene with 10 ml of thionyl chloride and a few drops of pyridine. After the mixture was stirred for 4 hr at 25° and 1 hr at 45°, the solvent and excess thionyl chloride were removed under reduced pressure. An additional 40 ml of benzene was added, and the solution was distilled under reduced pressure to remove the final traces of thionyl chloride. The diacid chloride was dissolved in 100 ml of ether and filtered through glass wool. The ether solution was then added to an ethereal solution of diazomethane (prepared from 33 g of Diazald) at 0°. After the solution was slowly warmed to 25° and left to stand for 12 hr the ether was removed under reduced pressure to give the crude bis(diazo) ketone (*caution:* potentially explosive). The bis(diazo) ketone was dissolved in 50 ml of methanol to which a mixture of 0.5 g of silver acetate in 5 ml of triethylamine was added slowly with stirring. After the evolution of nitrogen was complete, the solution was heated to reflux, decolorized with charcoal, and filtered, and the solvent was removed under reduced pressure to yield the crude diester. The diester was dissolved in 100 ml of ether, and the solution was washed with 2 *N* hydrochloric acid and 10% sodium bicarbonate and then dried over $MgSO_4$. Filtering and evaporation of the ether under reduced pressure gave 2.1 g of diester which was purified by glpc (5 ft × 0.25 in. columns) using 10% QF-1, 15% FFAP, 15% Carbowax 20M, or 20% DEGS columns at 160-200°: pmr (CCl_4) δ 3.60 (s, 6), 2.45-2.10 (t, 4, J = 7 Hz), 2.1-1.0 (m, 5), 1.0-0.85 (m, 3); mass spec (70 eV) *m/e* (rel intensity) 202 (1), 171 (21), 143 (3).

Using the above procedure, 0.5 g of 3,3-dimethylglutaric acid yielded 200 mg of **dimethyl 4,4-dimethylpimelate:** pmr (CCl_4) δ 3.60 (s, 6), 2.4-1.95 (m, 4), 1.75-1.3 (m, 4), 0.88 (s, 6); mass spectrum (70 eV) *m/e* (rel intensity) 216 (1), 185 (15), 157 (7). **Dimethyl 3-methylpimelate** (3.4 g) was obtained from 3.7 g of the glutaric ester; pmr (CCl_4) δ 3.60 (s, 6), 2.5-2.0 (m, 4), 1.9-1.05 (m, 3); mass spectrum (70 eV) *m/e* (rel intensity) 202 (1), 171 (25), 143 (4).

The above procedure yielded 2.4 g of a mixture of *meso*- and *rac*-dimethyl 3,5-dimethylpimelate from 3.6 g of a mixture of *meso*- and *rac*-2,4-dimethylglutaric acids. The pimelate esters were hydrolyzed, and the meso diacid was separated from the racemic isomers by benzene extraction. The less soluble racemic isomer was recrystallized from benzene (50%)-acetone (50%) to give 350 mg of *dl*-3,5-dimethylpimelic acid, mp 136-138° (lit.[38] mp 139-140°). *meso*-3,5-Dimethylpimelic acid (120 mg, mp 75-82°) was obtained by fractional crystallization from benzene (75%)-ethyl acetate (25%). Both isomers were esterified with the boron trifluoride-methanol complex.[33] **Dimethyl *d,l*-3,5-dimethylpimelate** gave pmr (CCl_4) δ 3.60 (s, 6), 2.3-1.65 (m, 1), 1.3-1.05 (m, 2), 1.05-0.05 (d, 6, J = 6.5 Hz); mass spectrum (70 eV) *m/e* (rel intensity) 216 (1), 185 (25), 157 (3). **Dimethyl *meso*-3,5-dimethylpimelate** gave pmr (CCl_4) δ 3.60 (s, 6), 2.4-1.7 (m, 2), 1.05-0.85 (d, 6, J = 6.5 Hz); mass spectrum (70 eV) *m/e* (rel intensity) 210 (1), 185 (15), 157 (3). The fine structure of the ir and pmr spectra of the two isomers was distinctively different. **Dimethyl *erythro*-3,4-dideuteriopimelate** was prepared by the addition of deuteriodiborane to 1,4-cyclohexadiene followed by oxidation and chain extension to a mixture of 16 g of 1,4-cyclohexadiene, 50 g of diglyme, and 2 g of lithium aluminum deuteride to which was added 75 mmol of boron trifluoride etherate over a period of 1 hr.[39,40] The solution was stirred an additional 30 min before the addition of 20 g of acetic-*d* acid. After the solution was heated to reflux for 2 hr, the product slowly distilled. Redistillation gave 3.5 g of a ~1:1 mixture of the diene and dideuteriocyclohexene which was oxidized without separation by the addition of 180 g of potassium permanganate to the olefins dissolved in 1.5 l. of acetone by the general procedure described previously. The desired **dimethyl *meso*-3,4-dideuterioadipate** was purified by glpc (15% Carbowax 20M at 150°) to give 0.6 g of product: pmr (CCl_4) δ 3.60 (s, 6), 2.45-2.15 (m, 4), 1.75-1.45 (m, 2^+). Repeated integration indicated at least 90% deuterium incorporation. The adipate (0.5 g) was refluxed in 50 ml of methanol containing an equimolar amount of sodium hydroxide for 4 hr giving a mixture of products including the desired half ester. Acidification, ether extraction, drying, and solvent evaporation left a crude product which was chain extended by the Arndt-Eistert procedure described previously. The crude dimethyl *erythro*-3,4-dideuteriopimelate was purified by glpc using a Carbowax 20M column at 160° to give 0.2 g of product: pmr (CCl_4) δ 3.60 (s, 6), 2.45-2.10 (m, 4), 1.90-1.25 (m, 4^+). Conversion of this ester to the cycloheptanesemidiones gave a mixture of **8j** and **8k** having a^H = 6.60 (2), 2.05 (1), 0.54 (1), 0.28 (4), a^D = 0.32 (**8k**), and a^H = 6.60 (2), 2.05 (2), 0.28 (3) G (**8j**). These hfsc require the 2.1-G interaction at C-4,6 and the 0.5-G interaction at C-5 to be from equatorial hydrogen atoms as demanded by the chair but not the boat conformation.

Preparation of Precursors to 17, 18, 27, 28. The bicyclo[2.2.2]octane derivatives were prepared from the Diels-Alder adduct of cycloheptatriene and maleic anhydride **41**: mp 101-101.5° (lit.[41] mp 101°); pmr ($CDCl_3$) δ 6.00-5.76 (m, 2), 3.62-3.33 (m, 2), 3.33-3.17 (m, 2), 1.30-0.97 (m, 2), 0.58-0.18 (m, 2). Reduction of **41** in C_6H_6 at 1 atm with Pd/C catalyst gave the saturated anhydride, mp 139-140° (lit.[42] mp 140°). Treatment of the saturated anhydride with aqueous $NaHCO_3$ at 70° followed by acidification gave the diacid, mp 185-186° dec. ***exo*-Tricyclo[3.2.2.$0^{2,4}$] non-6-ene,** precursor to **17,** was prepared by bisdecarboxylation of 60 g (0.286 mol) of the diacid with 160 g (0.362 mol) of lead tetraacetate in benzene (550 ml)-pyridine (65 ml). The desired olefin was sublimed [100° (2 Torr)] from the reaction products to give 7.6 g (22%) of the desired product: pmr (CCl_4) δ 0.3-1.6 (multiplets, 8) 2.58 (m, 2), 6.4 (m, 2). The olefin was oxidized by permanganate, esterified by diazomethane, and converted to the bis(trimethylsiloxy)alkene without isolation of intermediates.

Isomeric semidiones **18** and **28** were prepared by the Simmons-Smith reaction of tricyclo[3.2.2.$0^{2,4}$]octa-6,8-diene prepared by anodic oxidation of **41.**[43] The diene had pmr (CCl_4) δ 6.65-6.35 (m, 2), 6.05-5.75 (m, 2), 3.75-3.43 (m, 2), 1.30-0.95 (m, 2), 0.78-0.20 (m, 2). The diene (2.7 g) was reacted with 9 g of methylene and 3.6 g of the zinc-copper couple at reflux for 3 hr to give 2.2 g of a mixture of olefins, bp 95-100° (15 Torr). Upon oxidation with 8.6 g of potassium permangante in 150 ml of acetone buffered with 0.5 g of sodium bicarbonate, the mixture was converted to *trans*-tricyclo[5.1.0.$0^{3,5}$]octane-*cis*-2,6-dicarboxylic acid which was esterified by boron trifluoride-methanol and purified by glpc on a 10% QF-1 column at 150° to give 240 mg of dimethyl ***trans*-tricyclo[5.1.0.$0^{3,5}$]octane-*cis*-2,6-dicarboxylate** (precursor to **18**): mp 63.5-66.0°; pmr (CCl_4) δ 3.60 (s, 6), 2.40-2.20 (m, 2), 1.60 to −0.35 (m, 8); mass spectrum (70 eV) *m/e* (rel intensity) 224 (10), 193 (5), 165 (60). Distillation of the acetone used as the solvent for oxidation led to the recovery of 1.2 g of the ***endo,endo*-tetracyclo[3.3.2.$0^{2,4}$.$0^{6,8}$]dec-9-ene** which served as a precursor to **28** by use of the benzoyl nitrite route of Scheme V.

Precursors to **27** were prepared from **41** by reduction in refluxing ether with lithium aluminum hydride (30 hr) to give ***syn,syn*-8,9-dimethanol-*endo*-tricyclo[3.2.2.$0^{2,4}$]non-6-ene:** mp 113-114° (recrystallized from C_6H_6); pmr ($CDCl_3$) δ 0.18-0.16 (m, 2), 0.93 (m, 2), 2.22 (m, 2), 2.65 (m, 2), 3.50 (m, 4) 4.57 (2, 2, exchanged with D_2O), 5.61 (m, 2).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.25; H, 8.95.

In pyridine solution, the diol was converted to the ditosylate; mp 93.5-94.5° (recrystallized from methanol); pmr ($CDCl_3$) δ −0.14-0.3 (m, 2), 0.87 (m, 2), 2.33 (m, 2), 2.43 (s, 3), 2.80 (m, 2), 3.79 (m, 4), 5.54 (m, 2), 7.34 (d, 4, J = 8 Hz), 7.78 (d, 4, J = 8 Hz). The ditosylate was reduced with lithium aluminum hydride in refluxing ether (70 hr) to give ***syn,syn*-8,9-dimethyl-*endo*-tricyclo[3.2.2.$0^{2,4}$]non-6-ene:** bp 85-87° (15 Torr); pmr (CCl_4) δ 0.24-0.33 (m, 2), 0.6-1.16 (m, 2), 0.81 (d, 6, J = 7 Hz), 1.98 (m, 2), 2.52 (m, 2), 5.71 (m, 2).

Anal. Calcd for $C_{11}H_{10}$: C, 89.12; H, 10.88. Found: C, 84.80, 84.85; H, 9.96, 10.08. Hydroboration of the olefin gave the alcohol, mp 74-75°, which was oxidized by chromium trioxide in pyridine in 9 hr at 25° to ***syn,syn*-8,9-dimethyl-*endo*-tricyclo[3.2.2.$0^{2,4}$]nonan-6-one** purified by glpc (15% Carbowax 20M, 164°): ir (neat) 1718 cm^{-1}; pmr (CCl_4) δ 0.0-2.5 (multiplets); mass spectrum (20 eV) *m/e* 164(M^+), 149(m − 15), 136(m − 28), 131(m − 33), 115(m − 49), 107(m − 57), 92(m − 72). The ketone could be oxidized to **27** in basic DMSO solutions, but a better esr spectrum was obtained from the olefin by the benzoyl nitrite route (Scheme V).

6,7-Dichloro-*endo*-tricyclo[3.2.2.$0^{2,4}$]nonane-*endo*-6,7-dicarboxylic Anhydride. Precursor of 23. Cycloheptatriene (9.2 g, 0.1 mol) and dichloromaleic anhydride (16.7 g, 0.1 mol) in 10 ml of xylene were heated in a glass tube for 2 days at 170°. Upon cooling of the solution, white crystals were formed which were recrystallized from acetic acid and sublimed at 110° (0.2 Torr) to give **6,7-dichloro-*endo*-tricyclo[3.2.2.$0^{2,4}$]-9-nonene-*endo*-6,7-dicarboxylic anhydride,** mp 154-155°.

Anal. Calcd for $C_{11}H_8Cl_2O_3$: C, 51.0; H, 3.11; Cl, 27.4. Found: C, 50.9; H, 3.12; Cl, 27.4.

The unsaturated tricyclic anhydride was reduced in acetic acid with 10% Pd on carbon at 25° (1 Torr) until 1 mol of hydrogen had been absorbed (3 hr). Recrystallization from ether gave material: mp 178–179°; pmr ($CDCl_3$) δ 0.75–1.05 (m, 2), 1.10–1.70 (m, 6), 2.75–2.95 (m, 2).

Anal. Calcd for $C_{11}H_{10}Cl_2O_3$: C, 50.6; H, 3.86; Cl, 27.2 Found: C, 50.6; H, 3.82; Cl, 27.7.

***endo*-Tricyclo[3.2.2.0^{2,4}]non-6-ene. Precursor to 26.** The olefin was prepared by the addition of cyclopropene to 1,3-cyclohexadiene[44a,b] using the procedure published for cyclopentadiene.[44c] To a stirred suspension of 30 g of sodium amide in 50 ml of mineral oil at 90° under nitrogen was added 50 ml of allyl chloride in 30 ml of mineral oil over an 8-hr period. The generated cyclopropene was passed into a solution of 5 g of 1,3-cyclohexadiene in 45 ml of pentane under a Dry Ice condenser. After the addition was complete, the solution was stirred for 2 hr before bulb-to-bulb vacuum distillation (0.5 Torr) gave 1.3 g of the desired olefin contaminated with ~20% of cyclohexadiene. Purification by glpc (15% Carbowax 20M, 120°) gave the pure olefin: mp 59–60.5° (lit.[43a] mp 54°); pmr (CCl_4) δ 5.90–5.57 (m, 2), 2.83–2.50 (m, 2), 1.73–0.96 (m, 4), 0.96–0.60 (m, 2), 0.08 to −0.27 (m, 2). Oxidation of the crude olefin (1.8 g) with 7 g of potassium permanganate in acetone as described previously gave 1.6 g of the crude acid which was esterified with boron trifluoride–methanol complex to give 1.4 g of **dimethyl bicyclo[4.1.0]heptane-*endo,endo*-2,5-dicarboxylate** purified by glpc (Carbowax 20M, 190°): pmr (CCl_4) δ 3.60 (s, 6), 3.0–2.6 (m, 2), 1.9–1.1 (m, 6), 0.75–0.25 (m, 2); mass spectrum (70 eV) *m/e* (rel intensity) 212 (6), 181 (2), 153 (7).

Tricyclo[8.2^{1,5}.1^{3,7}]undecan-9-one. Precursor of 19. The ketone was prepared from 1.1 g of adamantanone[45] in 18 ml of methanol by the addition of 200 ml of an ether solution of diazomethane prepared from 20 g of Diazald. The resulting solution was stored at 0° for 5 days before evaporation of the solvent, and sublimation of the residue gave 600 mg of crude product which was further purified by glpc (SF-96 column at 160°) to give the desired ketone; mp 260°; pmr (CCl_4) δ 2.40, 2.05, 1.80 (all broad multiplets).

Preparation of Precursors to 22. The Diels–Alder adduct of cyclooctatetraene and maleic anhydride, mp 163–166° (lit.[46] mp 164–166°), was converted to the dimethyl ester, mp 50.0–52.5° (lit.[45] mp 52–55°), and photolyzed to **dimethyl pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decane-*cis*-9,10-dicarboxylate** according to the literature procedure,[47] mp 79–82° (lit.[46] mp 81–82°). Rearrangement catalyzed by silver nitrate according to the literature gave **dimethyl pentacyclo[4.4.0.0^{2,4}.0^{3,8}.0^{5,7}]decane-*cis*-9,10-dicarboxylate,** mp 102–104° (lit.[46] mp 104°), with a pmr spectrum identical with the reported value. The diester was converted to a semidione without isolation of the intermediate bis(trimethylsiloxy)alkene.

Preparation of Precursors to 30 and 36. *cis*-1,2-Cyclopropanediacetic acid was prepared,[48] mp 128–130° (lit.[47] mp 131–133°). The diacid was treated with diazomethane in methanol to yield **dimethyl cyclopropane-*cis*-1,2-diacetate:** bp 93–95° (0.5 Torr); pmr (CCl_4) δ 3.56 (s, 6), 2.45–1.95 (m, 4), 1.7–0.5 (m, 3), 0.10 to −0.25 (m, 1); mass spectrum (70 eV) *m/e* (rel intensity) 186 (1), 155 (14), 127 (40).

The diester precursors to **36a,b,c** were prepared from the bicyclo[2.2.1]heptenes according to Scheme II. Norbornene was oxidized to *cis*-1,3-cyclopentanedicarboxylic acid by a literature method,[49] (mp 119.9–120.6°). Using the procedure employed for conversion of glutaric acids to pimelic acids, 8.3 g of *cis*-1,3-cyclopentanedicarboxylic acid was chain extended to give 7 g of **dimethyl *cis*-1,3-cyclopentanediacetate** (precursor to **36a**): bp 107–112° (0.5 Torr); pmr (CCl_4) δ 3.60 (s, 6), 2.50–0.60 (m, 12); mass spectrum (70 eV) *m/e* (rel intensity) 214 (1), 183 (20), 165 (6).

anti- (85%) and *syn*- (15%) 7-deuteriobicyclo[2.2.1]heptane[50,51] were prepared by the reaction of tri-*n*-butyltin deuteride with *syn*-7-bromobicyclo[2.2.1]heptene.[5a] The olefin was converted to the cyclopentanedicarboxylic acid and then to **dimethyl *trans*- (85%) and *cis*- (15%) 2-deuterio-*cis*-1,3-cyclopentanediacetate,** precursor to **36b.** The pmr and mass spectra were consistent with the incorporation of one deuterium atom in the molecule. As a further check on the hfsc assigned to **36b,** the 85:15 mixture of dimethyl 2-deuterio-*cis*-1,3-cyclopentanedicarboxylates were refluxed in methanol containing 0.2 *M* in sodium methoxide for 24 hr to give dimethyl *trans*- (50%) and *cis*- (50%) 2-deuterio-*cis*-1,3-cyclopentanecarboxylate which was converted to the dimethyl-2-deuterio-*cis*-1,3-cyclopentanediacetate having the expected pmr and mass spectra and esr spectrum for the derived semidiones.

exo,exo-5,6-Dimethylbicyclo[2.2.1]hept-2-ene[24] was oxidized and chain extended to give **dimethyl *trans,trans*-2,3-dimethylcyclopentane-*cis*-1,4-diacetate** (precursor to **36c**) purified by glpc (10% QF-1 column at 180°): pmr (CCl_4) δ 3.60 (s, 6), 2.40–2.10 (m, 4), 2.10–1.40 (m, 5), 1.10–0.75 (m, 7); mass spectrum (70 eV) *m/e* (rel intensity) 242 (1), 211 (8), 183 (1).

Synthesis of Bicyclo[3.2.2]non-6-ene Precursors to 37a,b. The cycloheptadiene–maleic anhydride Diels–Alder adduct **39** was prepared,[42] mp 102–104° (lit.[42] mp 110–111°). The unsaturated anhydride **39** was hydrogenated by 10% Pd/C in ethyl acetate to give **bicyclo[3.2.2]nonane-*endo,cis*-6,7-dicarboxylic anhydride,** mp 152–155° (lit.[42] mp 156–157°). The anhydride was refluxed in methanol containing a trace of acid for 10 hr before addition of 500 ml of 1 *N* aqueous sodium hydroxide. The methanol was distilled and the aqueous solution refluxed 4 hr before cooling and acidification with sulfuric acid. The diacid was extracted with ether and dried, and the ether was distilled under reduced pressure. The crude diacid fraction was added to 80 g of lead tetraacetate in 500 ml of pyridine and heated to 75° for 30 min. Acidification to congo red with dilute nitric acid afforded 6.6 g of olefin isolated by ethereal extraction. Purified **bicyclo[3.2.2]non-6-ene** by glpc had: mp 107–108°; pmr (CCl_4) δ 6.15–5.95 (m, 2), 2.60–2.20 (m, 2), 1.85–1.30 (m, 10). The olefin (5 g) was oxidized for 20 hr by 12 g of potassium permanganate in 215 ml of water containing 2.7 g of ammonium sulfate. The aqueous solution was filtered, concentrated to 50 ml, acidified, and extracted with ether to give the diacid which was esterified with diazomethane to give **dimethyl *cis*-1,4-cycloheptanedicarboxylate,** precursor to **37a.** The diester was also treated with methanol-*d*–sodium methoxide to give dimethyl **1,4-dideuterio-*cis*-1,4-cycloheptanedicarboxylate** which gave the expected esr spectrum.

The unsaturated anhydride **39** was converted to **37b** by lithium aluminum hydride reduction in ether to give **bicyclo[3.2.2]non-6-ene-*endo,cis*-8,9-dimethanol:** mp 65.5–67.5°; pmr ($CDCl_3$) δ 6.10–5.85 (m, 2), 3.75–3.40 (m, 6), 2.55–2.15 (m, 4), 1.65–1.40 (m, 6). This diol was converted by *p*-toluenesulfonyl chloride in pyridine to the ditosylate derivative: mp 90–91°; pmr ($CDCl_3$) δ 7.90–7.65 (d, 4, *J* = 8.4 Hz), 7.45–7.20 (d, 4, *J* = 8.4 Hz), 5.95–5.75 (m, 2), 4.00–3.70 (m, 4), 2.55–2.20 (m, 10), 1.65–1.20 (m, 6). Reduction with lithium aluminum hydride in ether gave ***endo, cis*-8,9-dimethylbicyclo[3.2.2]non-6-ene:** pmr (neat) δ 6.15–5.90 (m, 2), 2.30–1.90 (m, 4), 1.65–1.35 (m, 6), 1.00–0.80 (m, 6). The olefin (5.8 g) was oxidized by 22 g of potassium permanganate in 500 ml of acetone containing 1.6 g of sodium bicarbonate according to the previously described procedure, and the resulting diacid was esterified with boron trifluoride–methanol complex to yield **dimethyl *cis,cis*-2,3-dimethylcycloheptane-*cis*-1,4-dicarboxylate,** precursor to **37b.**

Dimethyl 1,5-Cyclooctanedicarboxylate, Precursor of 40. The reaction sequence of Scheme IV was followed using the procedure of Cope.[53,54] **β-(1-Carbethoxy-2-ketocyclohexyl)propionaldehyde,** bp 109–112–112° (0.2 Torr), was converted to **1-carbethoxybicyclo[3.3.1]non-3-en-9-one,** mp 45.5–46.5° (lit.[52] mp 48.5–49.5°), and then to **diethyl 1,5-cyclooctenedicarboxylate:**[53] pmr (CCl_4) δ 7.10–6.70 (t, 1, *J* = 8 Hz), 4.40–3.80 (m, 4), 2.70–1.45 (m, 11), 1.45–1.05 (m, 6). Saponifications yielded the diacid, mp 208–214° (lit.[53] mp 217.5–219.5°). The unsaturated diacid was hydrogenated in acetic acid with 10% Pd/C. Filtration and distillation of the solvent left a crude cis–trans mixture of diacids which was converted to the cis anhydride by refluxing with acetic anhydride for 4 hr. Final esterification by methanol and a trace of acid gave **dimethyl 1,5-cyclooctanedicarboxylate,** mp 39–46°, purified by glpc (10% QF-1 column, 190°): pmr (CCl_4) δ 3.58 (s, 6), 2.65–2.15 (m, 2), 2.15–1.35 (m, 12); mass spectrum (70 eV) *m/e* (rel intensity) 228 (1), 197 (12), 169 (37).

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Aliphatic Semidiones. XXX. Alkenyl and Cycloalkyl Substituted 1,2-Semidiones[1]

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Abstract: The esr spectra of a series of cycloalkyl (C_3–C_8) substituted semidiones are reported and hyperfine splitting constants are assigned. The bisected conformation is highly preferred for cyclopropyl and other cycloalkyl substituted semidiones, including the anti($n + 3$)-position derivatives of the bicyclo[n.1.0]alkanes. The rigid geometry of the latter radical anions gives rise to unusually large long range interactions involving 4 and 5 bonds in a zigzag coplanar arrangement with a carbon p_z orbital in the semidione spin label. Alkenyl semidiones with α,β-unsaturation have a high spin density at the β position ($\rho_{C-\beta} \approx 0.2$) and are highly reactive. However, cis-trans isomerization about α,β-conjugated double bonds cannot be detected.

Biscycloalkyl-1,2-semidiones. A series of acyloins (**1**) and semidiones (**2**) were prepared from the corresponding cycloalkanecarboxylic esters.

Somewhat simpler esr spectra were obtained from the methylcycloalkylsemidiones (**4**) obtained from the acyloins (**3**) prepared either by a mixed acyloin condensation (**3a, c**) or by addition of methylmagnesium bromide to the carboxaldehyde cyanohydrins.

Figure 1 gives typical esr spectra for **2c** and **4c**. The observed hfsc are collected in Table I.

The semidiones **2** and **4** show several conformational effects as well as new examples of long range splitting. We have commented previously on the highly preferred bisected conformation of cyclopropyl substituted semidiones[3] and acyclic secondary alkyl substituted semidiones,[4,5] where $a_\alpha{}^H \sim P_c\langle\cos^2\theta\rangle$. Bulkier substituents (R′ in **5**, Scheme I) cause a decrease in the value of $a_\alpha{}^H$ indicating a decrease in torsional motion ($\pm\theta$) as the bulk of R′ is increased. The value of $\langle\cos^2\theta\rangle$ appears to be quite constant for **2c–g** (or **4c–h**) and about equal to the value for *trans*-diisopropylsemidione, where $a_\alpha = 2.0$ G. There does seem to be an additional electronic factor leading to a lower value of $a_\alpha{}^H$ for the cyclopropyl substituted semidiones **2a, 4a, 2i, 2j, 4j** and **4k**. This interaction does not lead to an enhanced value of