Aliphatic Semidiones. XIX. Polycyclic Derivatives of Cyclobutanesemidione[1]

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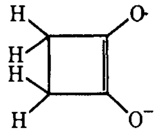
Abstract: Bicyclo[3.2.0]heptane-6,7-semidione, bicyclo[4.2.0]octane-7,8-semidione, bicyclo[4.2.0]oct-3-ene-7,8-semidione, and a number of their tri-, tetra-, and pentacyclic derivatives have been examined by electron spin resonance spectroscopy. A number of long-range hyperfine splittings have been observed and assigned. The conformations of the bicyclic systems appear to be staggered involving the cis-fused cyclohexane or cyclohexene rings in a boat. Extended Hückel MO calculations and ^{13}C natural abundance splittings are reported for some semidiones.

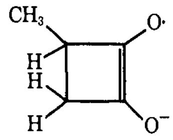
Cyclobutanesemidione (**1**) can be prepared by treatment of the α-hydroxy ketone with base in DMSO or DMF.[6] The acyloin condensation of *cis*-1,2-dicarboxylic esters by sodium–potassium alloy (NaK) in 1,2-dimethoxyethane (DME) followed by treatment of the unisolated acyloin with base in DMSO is a convenient route to cyclobutanesemidione and many of its derivatives.[7] When the acyloin condensation is performed in the presence of trimethylchlorosilane,[8] the resulting 1,2-bis(trimethylsiloxy)cyclobutenes can be isolated and then converted to the semidiones by the action of potassium *tert*-butoxide in DMSO.[9]

The cyclobutene ring in **1** and various of its derivatives are very rigid spin labels and little effect of temperature[6] or of substitution is seen on the magnitude of $a_\alpha{}^H$ (*e.g.*, **1** and **1a**).



$a^H(4) = 13.85$ (DMSO); 14.40 G (DME)

1



$a^H(2) = 14.8$, $a^H(1) = 12.8$ G (DME)

1a

Cyclobutanesemidiones when fused into polycyclic systems appear to have a very favorable geometry for long-range interactions involving a zig-zag, approximately coplanar, arrangement of bonds and the carbonyl carbon p_z orbital.[10] Unfortunately, all attempts to prepare bicyclo[2.1.0]pentanesemidione or bicyclo-[2.2.0]hexanesemidione by the acyloin condensation method have failed. Under the conditions of the acyloin condensation a weak esr signal is detected for cyclopentane-1,2-semidione and cyclohexane-1,2-semidione from the *cis*-1,2-cyclopropane and *cis*-1,2-cyclobutane dicarboxylic esters.[11] Other workers have been unable to effect an acyloin condensation using the cyclobutane dicarboxylic esters.[12]

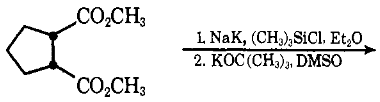
We have performed extended Hückel SCF–MO calculations, by a technique previously described[11] for the systems with the geometries shown in Figure 1. The calculated hfsc constants are given in Table I.

Table I. Calculated and Experimental Hyperfine Splitting Constants for Cyclobutanesemidiones

Semidione	θ, deg	$a_1{}^H$	$a_{2s}{}^H$	$a_{2a}{}^H$	$a_{3s}{}^H$	$a_{3a}{}^H$
1, expt		13.9				
1, calcd		15.4, 10.6[a]				
2, calcd	120	3.0	0.1	6.0		
2, calcd	115	2.1	0.1	8.5		
3, calcd	120	7.1	0.2	1.3		
3, calcd	115	5.3	0.5	2.0		
4, expt		12.8	0.06	0.62	0.30	0.62
4, calcd	120	14.9	0.6	0.9	0.4	0.9
4, calcd	115	11.8	1.4	2.1	0.3	1.0

[a] INDO calculation without gegenion. Use of Li^+ in the INDO calculation (geometry of Figure 1) yields $a^H = +9.9$ G.

The acyloin condensation of dimethyl *cis*-1,2-cyclopentanedicarboxylate gives a semidione (**4**) in which hfs by eight hydrogen atoms can be detected (Figure 2).



4

$a_\alpha{}^H = 12.8$ (2)
$a^H = 0.26$ (3)
$a^H = 0.30$ (1)
$a^H = 0.06$ (2)

The assignment of hfsc can be made by analogy with cycloheptane-1,2-semidione,[13] as $a^H = 0.62$ G for the trans (to the cyclobutene ring) hydrogen at C-2, C-4, and cis at C-3. The trans hydrogen at C-3 has $a^H = 0.3$ and the cis hydrogens at C-2 and C-4 have

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[3] National Science Foundation Predoctoral Fellow, 1967–1970.

[4] National Science Foundation Predoctoral Fellow, 1965–1969.

[5] National Science Foundation Undergraduate Research Participant, Summer 1970.

[6] G. A. Russell, G. R. Underwood, and D. C. Lini, *J. Amer. Chem. Soc.*, **89**, 6636 (1967).

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

[8] K. Rühlmann, H. Seefluth, and H. Becker, *Chem. Ber.*, **100**, 3820 (1967).

[9] G. A. Russell and P. R. Whittle, *J. Amer. Chem. Soc.*, **91**, 2813 (1969).

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

[11] G. A. Russell, P. R. Whittle, J. J. McDonnell, R. S. Givens, and R. G. Keske, *ibid.*, **93**, 1452 (1971).

[12] J. J. Bloomfield, R. G. Todd, and L. T. Takahashi, *J. Org. Chem.*, **28**, 1474 (1963).

[13] G. A. Russell and R. G. Keske, *J. Amer. Chem. Soc.*, **92**, 4458 (1970).

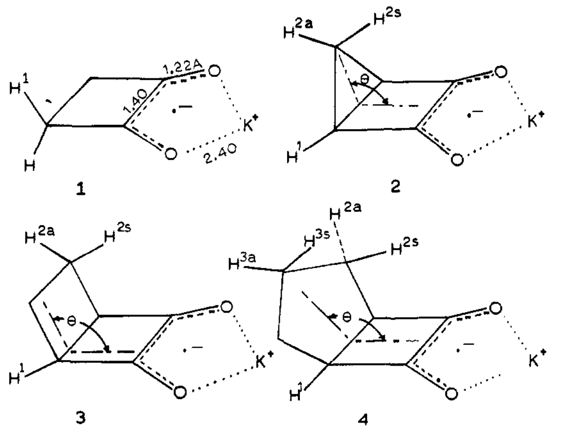
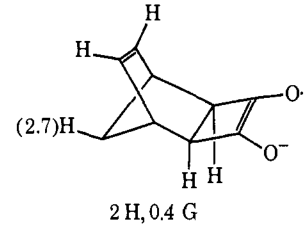


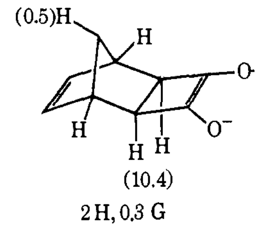
Figure 1. Geometry and numbering of cyclobutanesemidiones for MO calculations. All carbon–carbon single bonds were 1.54 Å, all carbon–hydrogen bonds 1.09 Å, and all H–C–H angles were taken as 111°. All rings were assumed to be planar. The methylene and methine hydrogen atoms were placed so that for a given group all H–C–C angles were equal.

a^H = 0.06 G. The conformation of **4** appears to be staggered as in the case of cycloheptanesemidione.

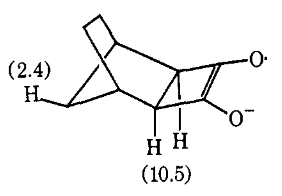
The tricyclo[4.2.1.0^{2,5}]non-7-ene-3,4-semidiones were prepared *via* the acyloin condensation of *cis-exo-* and *cis-endo-*norbornene dicarboxylates. The corresponding norbornane dicarboxylates yielded the saturated tricyclic semidiones. Semidiones **5** and **6** as well as **7** and **8** had grossly different esr spectra. The assignment of hfsc was partially proven for **8** by the synthesis of **9** and **10**.



2 H, 0.4 G
5



2 H, 0.3 G
6



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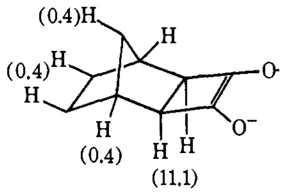

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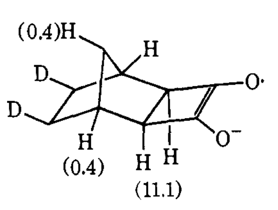

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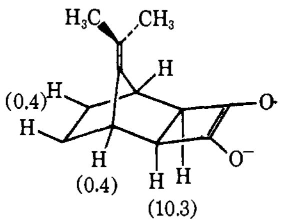


10

From the results observed for **8**–**10** it seems evident that the 0.3-G triplet observed for **6** should be assigned to the bridgehead hydrogens of the bicycloheptene.

Compound **11**, a pentacyclic derivative of **7**, was also examined. The assignment of the triplet splittings of ~0.4 G in **11a** to H_a seems straightforward when **11b** and **11c** are considered. The 0.16-G triplet in **11a** must be the result of interaction (3 V) with H_1.

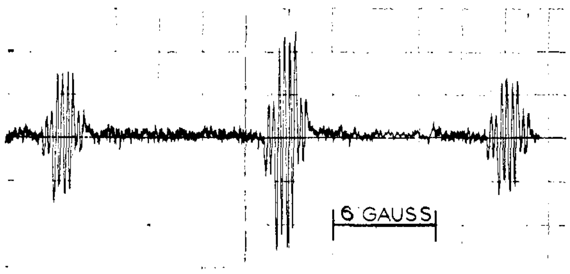
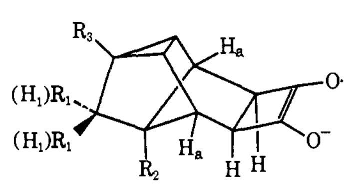
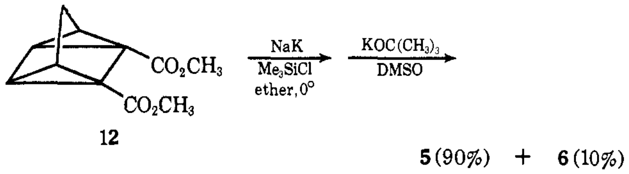


Figure 2. First-derivative esr spectrum of bicyclo[3.2.0]heptane-6,7-semidione (**4**) in DMSO solution at 25°, K^+ gegenion.

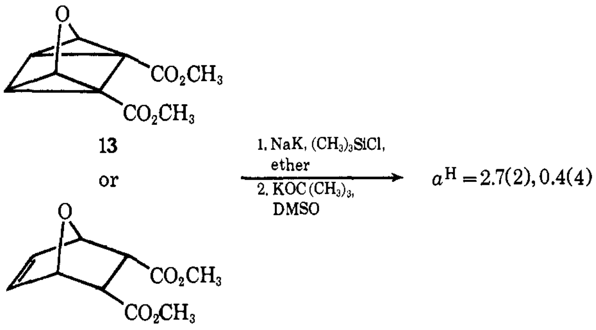


11a, $R_1 = R_2 = R_3 = H$; $a^H = 0.39(2), 0.16(2)$
b, $R_1 = R_3 = CH_3$; $R_2 = H$; $a^H = 0.37(2)$
c, $R_1 = R_2 = CH_3$; $R_3 = H$; $a^H = 0.40(2)$

Semidiones **5** and **6** were also produced as products of the acyloin condensation of diester **12**.[14] When the crude acyloin product was treated with base and DMSO-d_6 there was little incorporation of deuterium into **5** or **6**. The reductive ring opening of **12** apparently occurs during the acyloin condensation.



Diester **13**[14] gave an esr signal identical with that produced from diester **14**.



The product of these reactions is unknown but a possibility is the cyclooctatrienesemidione (**15**) with $a_\alpha^H > a_\beta^H, a_\gamma^H$.[15]

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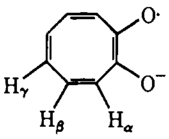
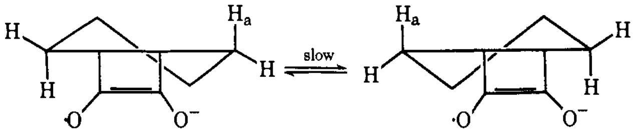
(14) Kindly supplied by Professor H. Prinzbach and Dr. G. Kaupp; see H. Prinzbach, *Pure Appl. Chem.*, 16, 17 (1968).

(15) Numerous attempts to produce **15** from cyclooctatrienone, cyclooctatetraene epoxide, or *cis*-1,2-dihydrophthalic esters have failed to yield any paramagnetic products. The diketone precursor to **15** is unknown. Hückel calculations predict a_α^H, $a_\gamma^H > a_\beta^H$, whereas

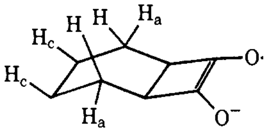


15

Semidiones **8–10** contain the bicyclo[4.2.0]octane-7,8-semidione ring system held in a rigid configuration in which the six-membered ring is forced to assume a boat conformation. However, the parent system could exist with the cyclohexane ring in either the half-chair (**16a**) or the boat conformation (**16b**). The semidione



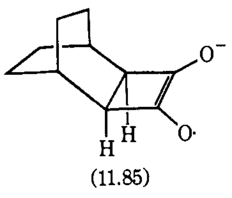
16a



16b

prepared from *cis*-1,2-cyclohexanedicarboxylic ester had a^H = 13.5 (2), 0.50 (2), and 0.25 (2) G. There was no pronounced effect of temperature on the spectrum. In **16b** the equatorial hydrogen atoms labeled H_a and H_c would most likely be responsible for the 0.5- and 0.25-G hfs. Such hfs values would be consistent with the values of a^H observed for **8–11**.

Semidiones **17–20** possess the bicyclo[4.2.0]octane-7,8-semidione nucleus with the cyclohexane ring forced into the boat structure by the ethano bridge between C-2 and C-5. A somewhat different splitting pattern is observed than for **8–10** when a methylene bridge existed between C-2 and C-5.



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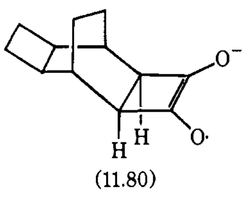

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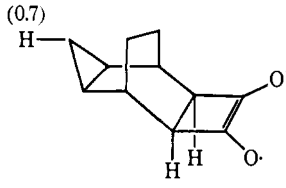

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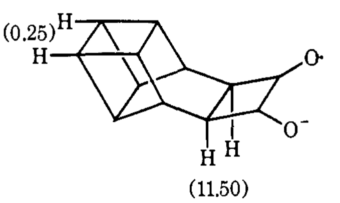
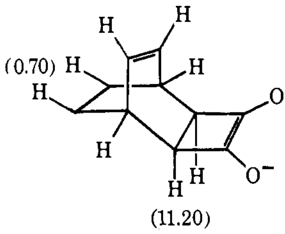


20

$a^H = 0.14(2)$

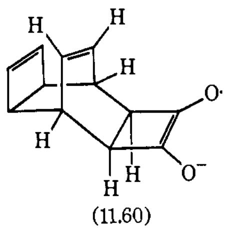
No long-range splittings were resolved in **17** or **18** because of wide line widths while for **19** only a long-range doublet splitting is observed. This doublet splitting is assigned as shown in the structure. The splitting involves a total of 3 V's between the hydrogen atom and the carbonyl carbon p_z orbital (heavy line in **19**). Semidione **20** also shows evidence of long-range splittings not detected in **17** or **18**. Two of the hydrogen atoms labeled in structure **20** form a 3 V–coplanar transoid arrangement of bonds with the carbonyl p_z orbital.

An ethylene bridge between C-2 and C-5 (**21–23**) of the bicyclo[4.2.0]octane-7,8-semidione nucleus presents still another hyperfine splitting pattern different from the methylene (**8**, **9**) or ethano bridges (**17–20**).



21

$a^H = 0.35(2)$



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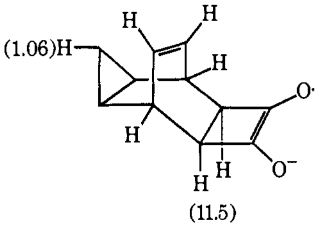
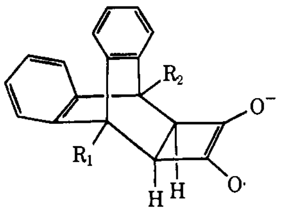
$a^H = 0.35(2)$



23

$a^H = 0.45(2), 0.15(2)$

The unassigned triplet splittings of 0.30–0.45 G in **5**, **6**, and **21–23** are believed to be at the bridgehead positions. This seems reasonable by analogy with **8–11** where these splittings have been proven. This assignment is also supported by the observed hfs in **24** and **25**.

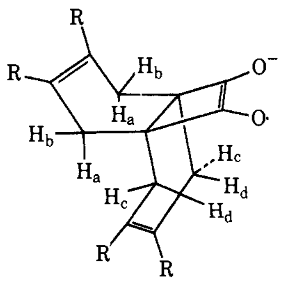


24a, $R_1 = R_2 = H; a^H = 10.75(2), 0.55(2)$

b, $R_1 = R_2 = D; a^H = 10.80(2)$

c, $R_1 = R_2 = CH_3; a^H = 10.55(2), 0.25(6)$

d, $R_1 = H; R_2 = CH_3; a^H = 10.65(2), 0.50, 0.25(3)$



25a, $R = H; a^H = 0.93(2), 0.46(6), 0.11(4)^{16}$

b, $R = CH_3; a^H = 0.87(2), 0.35(2), 0.28(4), a_{CH_3}{}^H = 0.07(2)$

INDO calculations using a tub conformation predict $a_\alpha{}^H$ is large (and positive) and $a_\beta{}^H$ and $a_\gamma{}^H$ are small (unpublished results of Mr. C. Chung).

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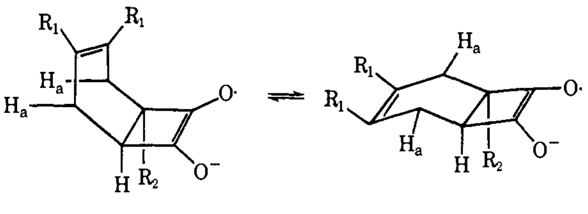
(16) J. M. Fritsch and J. J. Bloomfield, *Spectrosc. Lett.*, 1, 277 (1968).

For **25** we conclude that the vinyl hydrogen in both the boatlike and chairlike cyclooctadiene rings have $a^{H} = 0.11$ G. This leaves hfsc of ~0.9 (2) and ~0.5 (6) G to be assigned to the β-hydrogen atoms (H_a, H_b, H_c, H_d). Of these hydrogen atoms H_a exists in an excellent coplanar *W* plan arrangement with the carbonyl p_z orbitals and is assigned the 0.9-G hfsc.

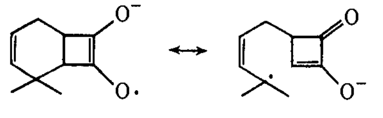
Our conclusions in regard to hfs in **5**, **6**, and **21–25** have implications in regard to $\Delta^{3,4}$-bicyclo[4.2.0]octane-7,8-semidione (**26**).[9] The semidione most reasonably exists in a boatlike or chairlike structure, or perhaps in a rapidly time-averaged mixture. However, there is no pronounced effect of temperature on the esr spectrum of **26** apparently excluding a time averaged mixture of conformations.



26a, $R_1 = R_2 = H$; $a^{H} = 13.5(2), 0.60(2), 0.35(2)$
b, $R_1 = CH_3$; $R_2 = H$; $a^{H} = 13.0(2), 0.70(2)$
c, $R_1 = H$; $R_2 = CH_3$; $a^{H} = 13.5, 1.20, 0.4(2), 0.20(3)$

The hfs values of **16** and **26a** or **26b** are very similar, perhaps suggestive of staggered conformations for both. The boatlike conformation for **26c** with $R_2 = CH_3$ seems definitely preferred since one H_a now has $a^{H} = 1.2$ G. In **25** H_a with a similar geometry has $a^{H} = 0.9$ G.

The hfs observed by hydrogen atoms attached to the β carbon atom in semidiones like **24–26** suggests the presence of spin density on the β-carbon atom as a result of hyperconjugation, *e.g.*, structure **27**.



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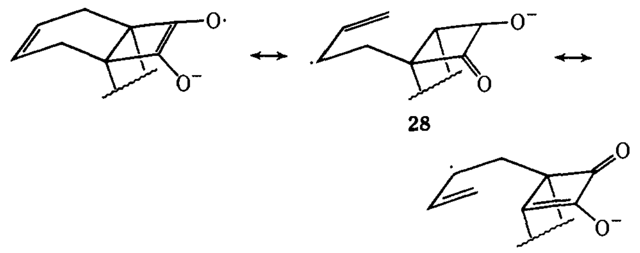
This explains the fact that at the bridgehead position of **24** a^{H} and $a_{CH_3}^{H}$ differ by only a factor of 2 (since $Q_{CH}^{H} \approx Q_{CCH_3}^{H}$). An alternate explanation for the values of a_{β}^{H} in **26c** involves the increased participation of **27** as a result of the presence of $R_2 = CH_3$ in the staggered conformation. Some experimental support for **27** has been obtained by the observation of natural abundance $a^{^{13}C}$ in **20**, **24**, and **26b**. Typical values of a^{C} for *cis*-semidiones are 1–1.5 G for a_{CO}^{C} and 5–6 G for a_{α}^{C} and a_{β}^{C}.[17] For cyclobutanesemidione we observed $a^{C} = 1.4$ and 5.4 G. In **24a–d** the values of a^{C} were 1.1 (CO), 5.1 (α), and 8.7 G. It appears that in accord with **27**, a_{β}^{C} is 8.7 G. For **20** we observed $a^{C} = 1.4$, 4.9, and 9.2 G while **26b** a^{C} was 1.5, 5.0, and 7.9 G. The observation that $a_{\beta}^{C} > a_{\alpha}^{C}$ in these bicyclic semidiones emphasizes the importance of delocalization of the unpaired electron in explaining long-range hydrogen splittings.

In **25b** we notice splitting by two of the vinyl methyls with $a_{CH_3}^{H} \approx a_{vinyl}^{H}$ for **25a**. A reasonable interpretation is that spin density has been transferred from the semidione spin label to one of the double bonds, *e.g.*, **28**. It is well known that $Q_{CH}^{H} \approx Q_{CCH_3}^{H}$.[18]



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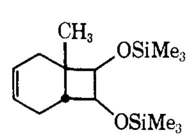
Semidiones **5–11**, **16–18**, **21**, **22**, and **26a** were prepared by the *in situ* acyloin condensation of the diesters in DME solution followed by dilution with a DMSO solution of potasssium *tert*-butoxide.[9] Semidiones **19**, **20**, **23**, **25b**, **26b**, and **26c** were prepared from the bis(trimethylsiloxy)alkenes and **25a** from the α-hydroxy ketone.[19] We have reported the preparation of **26c** by treatment of the three valence isomers **29–31**[20] with potassium *tert*-butoxide in DMSO.[9]



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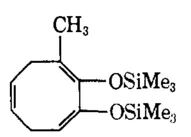

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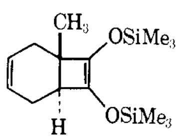

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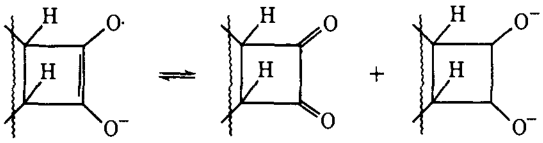
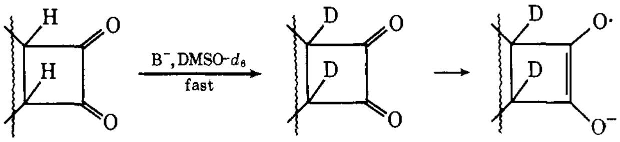
Facile hydrogen–deuterium exchange was observed for the α-hydrogen atoms of **16** and **26** in DMSO-d_6 in a process that was facilitated by the addition of small amounts of water. The initial exchanged species detected from **16** and **26** had exchanged both α-hydrogen atoms (as evidenced by the lack of any species with a doublet splitting of ~13.5 G). This result appears to implicate the diketone as a likely intermediate for the exchange process. Not all hydrogen–deuterium exchanges in semidiones involve the diketones. For example, the stereospecific exo exchange noted for the 4 position of bicyclo[3.1.0]hexane-2,3-semidione is retarded by water. Moreover, the stereoselectivity in itself seems to exclude the diketone as an intermediate for exchange and the dianion radical is thereby implicated.[11]





A few azacyclobutanedione radical ions were examined. Di-*tert*-butyl-1,2-diazetidinedione reacted with NaK in DME to give an esr spectrum with two nitrogen atoms, $a^{N} = 1.38$ G. Apparently **32** was formed. All attempts to prepare **33** or **34** from the acyloin condensation of the diesters failed to yield an esr signal in DMSO solution.

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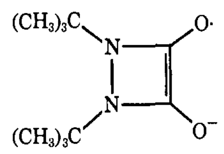

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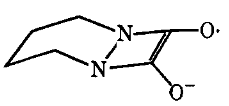

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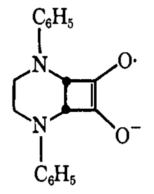

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Experimental Section

General Procedure for Generation of Semidiones. The *in situ* acyloin condensations were carried out by shaking a deaerated (with nitrogen) solution of the diester (0.4 *M*) in DME with a suspension of sodium-potassium alloy (1:1) in an equal volume of deaerated DME (about 120 mg of alloy/ml of DME), for about 1 min. In cases where extreme line broadening occurred, an aliquot of the solution was removed (under nitrogen) and mixed with an equal volume of a deaerated solution of potassium *tert*-butoxide (0.2 *M*) in DMSO. The admission of air to the latter solution often further improved the quality of the esr spectrum.

Semidiones were prepared from bis(trimethylsiloxy)alkenes by mixing equal volumes of well-deaerated solutions of the bis(trimethylsiloxy)alkene (0.2 *M*) and potassium *tert*-butoxide (0.4 *M*) in DMSO. In a typical experiment 1 ml of chlorotrimethylsilane followed by 0.1–0.2 mmol of the pure diester were added to a suspension of 0.2 ml of sodium-potassium alloy (1:3) in 25 ml of ether at 0° (nitrogen atmosphere). The mixture was stirred vigorously under nitrogen for 1–3 hr and filtered and the ether was removed *in vacuo*. The residue was taken up in 0.5 ml of DMSO, deaerated by bubbling nitrogen through the solution, and allowed to react with potassium *tert*-butoxide in DMSO as described above.

Dimethyl Methylsuccinate. Precursor of 1a. To a solution of 5.0 g of citraconic anhydride (Aldrich Chemical Co.) in 30 ml of methanol was added 0.2 g of sulfuric acid and the solution was refluxed for 36 hr. The methanol was removed *in vacuo* and the residue was dissolved in ether. The ethereal solution was extracted with saturated sodium bicarbonate solution, dried over magnesium sulfate, and concentrated to yield 6.0 g of dimethyl citraconate. To a solution of 2.0 g of this diester in 75 ml of benzene was added 0.6 g of 10% palladium on charcoal and hydrogen was bubbled through the stirred solution for 72 hr. The mixture was filtered and the filtrate was concentrated *in vacuo* leaving 2.0 g of crude product. An analytical sample of dimethyl methylsuccinate[21] was obtained by preparative glpc (15% Carbowax 20M, 155°); pmr (CCl_4) δ 1.18 (d, 3, J = 7 Hz), 2.20–3.10 (m, 3), 3.63 (s, 6).

Dimethyl *cis*-Cyclopentane-1,2-dicarboxylate. Precursor of 4. *cis*-1,2-Cyclopentanedicarboxylic anhydride, mp 69–70° (lit.[22] mp 70–72°), was esterified by refluxing with methanol containing a trace of sulfuric acid. The solution was diluted with ether and extracted with aqueous $NaHCO_3$ and by water. Removal of the ether under reduced pressure gave a product that was purified by glpc (20% DEGS, 150°) to give a 65% yield of the diester: pmr (CCl_4) δ 3.60 (s, 6), 3.25–2.90 (m, 2), 2.20–1.60 (m, 6); mass spectrum (70 eV) m/e (rel intensity) M^+ = 186 (1), 155 (100), 127 (20).

Dimethyl 5-Norbornene-*cis,endo*-2,3-dicarboxylate. Precursor of 5. This diester was prepared by the method of Bode:[23] pmr (CCl_4) δ 1.30–1.42 (m, 4), 3.18 (t, 2, J = 1.5 Hz), 3.50 (s, 6), 6.12 (t, 2, J = 1.5 Hz).

Dimethyl *cis,endo*-2,3-Norbornanedicarboxylate. Precursor of 7. To a solution of 500 mg of dimethyl 5-norbornene-*cis,endo*-2,3-dicarboxylate in 15 ml of dry benzene was added 100 mg of 10% palladium on charcoal; hydrogen was bubbled through the stirred solution for 18 hr. The mixture was filtered and the filtrate was concentrated *in vacuo*. An analytical sample of dimethyl *cis,endo*-2,3-norbornanedicarboxylate[23] was obtained by preparative glpc (20% DEGS, 195°): pmr (CCl_4) δ 1.20–1.90 (m, 6), 2.35–2.55 (m, 2), 2.80–2.90 (m, 2), 3.55 (s, 6).

Dimethyl 5-Norbornene-*cis,exo*-2,3-dicarboxylate. Precursor of 6. This diester was prepared by the method of Bode:[23] pmr (CCl_4) δ 1.40 (broad d, 1, J = 9 Hz), 2.10 (broad d, 1, J = 9 Hz), 2.51 (d, 2, J = 2 Hz), 3.02 (pentet, 2, J = 2 Hz), 3.57 (s, 6), 6.17 (t, 2, J = 2 Hz).

Dimethyl *cis,exo*-2,3-Norbornanedicarboxylate. Precursor of 8. Dimethyl 5-norbornene-*cis,exo*-2,3-dicarboxylate was hydrogenated in benzene in the presence of 10% palladium on charcoal to give dimethyl *cis,exo*-2,3-norbornanedicarboxylate.[23] An analytical sample was obtained by preparative glpc (20% DEGS, 195°): pmr (CCl_4) δ 1.05–1.70 (m, 5), 2.01 (broad d, 1, J = 10 Hz), 2.40–2.55 (m, 2), 2.58 (d, 2, J = 1.5 Hz), 3.51 (s, 6).

Dimethyl *cis,exo*-5,6-Dideuterionorbornane-*cis,exo*-2,3-dicarboxylate. Precursor of 9. Deuterium gas was bubbled through a stirred solution of 250 mg of dimethyl 5-norbornene-*cis,exo*-2,3-dicarboxylate and 50 mg of 10% palladium on charcoal in 15 ml of benzene for 24 hr. The suspension was filtered and the filtrate was concentrated *in vacuo*. An analytical sample of dimethyl *cis,exo*-5,6-dideuterionorbornane-*cis,exo*-2,3-dicarboxylate was obtained by preparative glpc (20% DEGS, 180°): pmr (CCl_4) δ 1.05–1.32 (m, 3), 2.04 (broad d, 1, J = 10 Hz), 2.49 (t, 2, J = 1.5 Hz), 2.60 (d, 2, J = 1.5 Hz), 3.52 (s, 6).

Dimethyl 7-Isopropylidine-*cis,exo*-2,3-norbornanedicarboxylate. Precursor of 10. 7-Isopropylidine-5-norbornene-*exo*-2,3-dicarboxylic anhydride was prepared by the procedure of Alder and Rühmann,[24] mp 134–135° (lit.[24] mp 137°), and converted to dimethyl 7-isopropylidine-5-norbornene-*cis,exo*-2,3-dicarboxylate, mp 74–76°, by refluxing with methanol and a trace of sulfuric acid. To a solution of 1.5 g of the unsaturated dimethyl ester in 50 ml of absolute ethanol was added 0.4 g of 10% palladium on charcoal and the mixture was shaken on a Parr Hydrogenator at 30 psi hydrogen pressure for 48 hr. The suspension was filtered and the solvent was removed *in vacuo*. The residue was recrystallized from hexane to give 1.4 g of dimethyl 7-isopropylidine-*cis,exo*-2,3-norbornanedicarboxylate: mp 104–106° (lit.[24] mp 114°); pmr (CCl_4) δ 1.20–1.70 (m, 4), 1.67 (s, 6), 2.67 (s, 2), 2.90 (t, 2, J = 2 Hz), 3.50 (s, 6); mass spectrum (70 eV) m/e 252 (M^+), 221, 193, 193, 192.

Dimethyl Tetracyclo[4.3.0.$0^{2,4}$.$0^{3,7}$]nonane-*endo,cis*-8,9-dicarboxylate. Precursor of 11a. 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;[25] mp 66–67° (lit.[26] mp 64°). Hydrogenation in benzene in the presence of 10% palladium on charcoal gave the saturated ester: mp 64–66° (lit.[26] mp 61–62°); pmr (CCl_4) δ 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).

Dimethyl 4,5,5- (and 5,5,6-) Trimethyltetracyclo[4.3.0.$0^{2,4}$.$0^{3,7}$]-nonane-*endo,cis*-8,9-dicarboxylate. Precursors of 11b,c. 1,7,7-Trimethylbicyclo[2.2.1]heptadiene[27] (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 ($CDCl_3$) δ 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) δ 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) M^+ = 278 (100), 247 (33), 219 (15). The nmr was indicative of the 5,5,6-trimethyl isomer, the precursor of **11c**.

The mother liquors from the recrystallization were evaporated to leave a semisolid residue which was eluted from a silica gel column by benzene–pentane (1:1). 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, precursor to **11b**: 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) M^+ = 278 (20), 247 (12), 219 (6).

Dimethyl *cis*-1,2-Cyclohexanedicarboxylate. Precursor of 16. Hexahydrophthalic anhydride (Aldrich Chemical Co.) was converted to dimethyl *cis*-1,2-cyclohexanedicarboxylate[28] by esterification with methanol and a trace of sulfuric acid. Vacuum distillation gave the pure diester: bp 93–94° (2 Torr) (lit.[27] bp 136° (18 Torr)); pmr (CCl_4) δ 1.12–2.13 (m, 8), 2.55–2.88 (m, 2), 3.60 (s, 6).

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Dimethyl *cis*-Bicyclo[2.2.2]octane-2,3-dicarboxylate. Precursor of 17. *cis*-Bicyclo[2.2.2]octane-2,3-dicarboxylic acid[29] was esterified with diazomethane in ether. An analytical sample of dimethyl *cis*-bicyclo[2.2.2]octane-2,3-dicarboxylate was obtained by preparative glpc (20% DEGS, 200°): pmr (CCl_4) δ 1.2–2.1 (m, 10), 2.80 (s, 2), 3.56 (s, 6).

Dimethyl *anti*-Tricyclo[4.2.2.0^{2,5}]decane-*cis*,*anti*-7,8-dicarboxylate. Precursor of 18. The unsaturated diester (precursor to **22**) was reduced with hydrogen and 10% palladium on charcoal. Recrystallization from hexane gave colorless needles of the saturated diester: mp 62–63° (lit.[29] mp 60–62°); pmr (CCl_4) δ 1.81 (s, 4), 1.90 (broad s, 2), 2.12 (d, 4), J = 4 Hz), 2.38 (m, 2), 2.62 (s, 2), 3.58 (s, 6).

Dimethyl *exo*-Tricyclo[3.2.2.0^{2,4}]nonane-*cis*-6,7-dicarboxylic Anhydride. Precursor of 19. The cycloheptatriene–maleic anhydride adduct, mp 100–101° (lit.[30] mp 101°), was hydrogenated to the saturated anhydride, mp 139–140° (lit.[31] mp 140°). The saturated anhydride (1.5 g) was refluxed in 50 ml of methanol containing 0.05 g of *p*-toluenesulfonic acid for 24 hr to yield 1.25 g of diester: mp 58–59°; nmr (CCl_4) δ 0.2–1.9 (m, 8), 2.23 (m, 2), 2.94 (broad s, 2), 3.58 (s, 6).

Dimethyl Pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decane-*cis*-9,10-dicarboxylate. Precursor of 20. This diester was prepared by the method of Dauben and Whalen.[32] The pure compound was obtained by chromatography on silica gel (elution with 5% ether–hexane), mp 81–82° (lit.[32] mp 81–82°).

Dimethyl *cis*,*endo*-Bicyclo[2.2.2]oct-5-ene-2,3-dicarboxylate. Precursor of 21. To 1.0 g of *endo*-bicyclo[2.2.2]oct-5-ene-2,3-dicarboxylic anhydride (Aldrich Chemical Co.) was added 0.5 ml of methanol and the mixture was refluxed for 4 hr. The excess methanol was removed and the residue was allowed to react with diazomethane (from 2.0 g of Diazald) in 50 ml of ether. The solution was extracted with 10% sodium hydroxide and saturated sodium chloride solutions and dried over magnesium sulfate, and the solvent was removed *in vacuo*. Recrystallization from ether–hexane gave 600 mg of white crystals: mp 69–71° (lit.[33] mp 69–71°); pmr (CCl_4) δ 1.1–1.8 (m, 4), 2.9 (broad s, 2), 3.00 (s, 2), 3.56 (s, 6), 6.30 (quartet, 2, J = 5 Hz, 3 Hz).

Dimethyl *endo*-Tricyclo[4.2.2.0^{2,5}]deca-3,7-diene-*cis*,*endo*-9,10-dicarboxylate. Precursor of 22. Tricyclo[4.2.2.0^{2,5}]deca-3,7-diene-*endo*-9,10-dicarboxylate anhydride was prepared by the method of Reppe, *et al.*[34] Reaction of this anhydride with methanol and a trace of sulfuric acid under reflux for 8 hr gave the corresponding diester: mp 51–52.5° (lit.[29] mp 52–55°); pmr (CCl_4) δ 2.70 (broad s, 2), 2.78 (s, 4), 3.52 (s, 6), 5.78 (s, 2), 5.90 (quartet 2, J = 4.5, 3 Hz).

Dimethyl *endo*-Tricyclo[3.2.2.0^{2,4}]non-6-ene-*cis*,*endo*-8,9-dicarboxylate. Precursor of 23. The cycloheptatriene–maleic anhydride adduct[30] was converted to the diester by methanol in the presence of *p*-toluenesulfonic acid: bp 135–140° (2 Torr); mp 66–67°; pmr (CCl_4) δ −0.41–0.20 (m, 2), 0.64 (m, 2), 2.72 (m, 4), 3.19 (s, 6), 5.46 (m, 2).

Dimethyl 9,10-Dihydro-9,10-ethanoanthracene-*cis*-11,12-dicarboxylate. Precursor of 24a. 9,10-Dihydro-9,10-ethanoanthracene-11,12-dicarboxylic anhydride[35] was refluxed with methanol and a catalytic amount of sulfuric acid for 21 hr to give the corresponding cis diester: mp 152–153° from hexane (lit.[36] mp 150–150.5°); pmr ($CDCl_3$) δ 3.20 (d, 2, J = 1.Hz), 3.49 (s, 6), 4.59 (d, 2, J = 1 Hz), 7.00–7.40 (m, 8); mass spectrum (70 eV) *m*/*e* 322 (M^+), 291, 263, 178.

Dimethyl 9,10-Dideuterio-9,10-ethanoanthracene-*cis*-11,12-dicarboxylate. Precursor of 24b. This compound was prepared from 9,10-dideuterioanthracene[37] by the same procedure as described for the 9,10-dihydro compound above. Upon recrystallization from benzene–hexane, colorless needles were obtained: mp 151–152°; pmr ($CDCl_3$) δ 3.19 (s, 2), 3.48 (s, 6), 7.00–7.40 (m, 8); mass spectrum (70 eV) *m*/*e* 324 (M^+), 293, 265, 180.

Dimethyl 9,10-Dimethyl-9,10-ethanoanthracene-*cis*-11,12-dicarboxylate. Precursor of 24c. 9,10-Dimethyl-9,10-ethanoanthracene-11,12-dicarboxylic anhydride[38] (1.0 g) was refluxed in 30 ml of methanol containing 0.2 ml of sulfuric acid for 21 days (reaction still incomplete). The unchanged anhydride was filtered off, the filtrate was concentrated, and the residue was dissolved in 50 ml of benzene. The solution was extracted with 10% sodium hydroxide and saturated sodium chloride solutions, dried over magnesium sulfate, and concentrated. Recrystallization from benzene–hexane gave 100 mg of colorless cubes: mp 211–214° (lit.[39] mp 209–211°); pmr ($CDCl_3$) δ 2.00 (s, 6), 3.06 (s, 2), 3.45 (s, 6), 7.00–7.45 (m, 8); mass spectrum (70 eV) *m*/*e* 350 (M), 319, 291, 206.

Dimethyl 9-Methyl-10-hydro-9,10-ethanoanthracene-*cis*-11,12-dicarboxylate. Precursor of 24d. 9-Methyl-10-hydro-9,10-ethanoanthracene-11,12-dicarboxylic anhydride,[36] mp 268–270° (lit.[36] mp 264–266°), was converted to the corresponding cis diester by refluxing in methanol with a trace of sulfuric acid for 42 hr: mp 165–167° (from benzene–hexane); pmr ($CDCl_3$) δ 1.93 (s, 3), 3.11 (d, 2, J = 1 Hz), 3.44 (s, 3), 3.48 (s, 3), 4.60–4.70 (m, 1), 7.00–7.55 (m, 8); mass spectrum (70 eV) *m*/*e* 336 (M^+), 305, 277, 192.

Dimethyl 3,4,8,9-Tetramethylbicyclo[4.4.0]decane-*cis*-1,6-dicarboxylate. Precursor of 25. The reaction of acetylenedicarboxylic acid with 2,3-dimethylbutadiene at 180° for 14 hr in the presence of hydroquinone gave a 45% yield of the anhydride.[40] The anhydride was hydrolyzed and esterified with diazomethane to yield the ester: pmr (CCl_4) δ 2.5 (s), 2.8 (s), 2.25 (broad s), 2.4 (broad s), 3.7 (s).

Dimethyl *cis*-Cyclohex-4-ene-1,2-dicarboxylate. Precursor of 26a. *cis*-Cyclohex-4-ene-1,2-dicarboxylic anhydride (Aldrich Chemical Co.) was refluxed with methanol containing a trace of sulfuric acid for 4 hr to give the corresponding cis diester: bp 93–94° (1.5 Torr) (lit.[41] bp 130–131° (14 Torr)); pmr (CCl_4) δ 2.25–2.54 (m, 4), 2.75–3.05 (m, 2), 3.60 (s, 6), 5.58 (t, 2, J = 1.5 Hz).

Dimethyl 4,5-Dimethylcyclohex-4-ene-*cis*-1,2-dicarboxylate. Precursor of 26b. 4,5-Dimethylcyclohex-4-ene-*cis*-1,2-dicarboxylic anhydride[42] was converted to dimethyl 4,5-dimethylcyclohex-4-ene-*cis*-1,2-dicarboxylate by refluxing with methanol and a trace of sulfuric acid. An analytical sample was obtained by preparative glpc (15% Carbowax 20M, 165°): pmr (CCl_4) δ 1.60 (s, 6), 2.15–2.45 (m, 4), 2.73–3.03 (m, 2), 3.60 (s, 6).

Dimethyl *cis*-1-Methylcyclohex-4-ene-1,2-dicarboxylate. Precursor of 26c. *cis*-1-Methylcyclohex-4-ene-1,2-dicarboxylic anhydride[43] was refluxed with methanol and a trace of sulfuric acid for 5 hr. Normal work-up and preparative glpc (15% Carbowax 20M, 155°) gave pure dimethyl *cis*-1-methylcyclohex-4-ene-1,2-dicarboxylate:[44] pmr (CCl_4) δ 1.18 (s, 3), 1.7–3.0 (m, 5), 3.58 (s 3), 3.61 (s, 3), 5.53 (broad s, 3).

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