Aliphatic Semidiones. XXXI. Conjugated Singly Unsaturated 1,2-Semidiones in Carbocyclic Systems[1]

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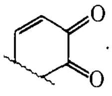
Abstract: The synthesis of conjugated unsaturated 1,2-semidiones in four-, five-, and six-membered rings has been investigated. Reaction of 5-acetoxy-4,4-dimethyl-2-cyclopenten-1-one and a variety of methyl-substituted 6-acetoxy-2-cyclohexen-1-ones with DMSO solutions of potassium *tert*-butoxide produced unsaturated 1,2-semidiones in the five- and six-membered rings. Since the lifetimes of some of these radicals were short, it was necessary to react the acetoxy ketones with basic DMSO solution under flow conditions. Benzo derivatives and heteroatom benzo derivatives of the unsaturated 1,2-semidione in the six-membered ring were also prepared. Oxidation of α- or β-tetralone produced 4-oxy-*o*-naphthosemiquinone which was also observed to be the final paramagnetic oxidation product from bullvalone, bicyclo[4.2.2]deca-2,4,7-trien-9-one, benzocyclohept-4-enone, 2,3-benzohepta-2,4-dienone, benzo[2.2.2]octadienone, and several of its valence isomers. In the presence of strong base several of the unsaturated acetoxy ketones produced the corresponding saturated semidiones by prototropic shifts. The ability of a sulfone group to impart stability to a cyclic 6π semiquinone system is reported.

The interpretation of electron spin resonance (esr) spectra of semidione radical anions (RC(O·)=C(O$^-$)R′) has been used for numerous conformational and structural assignments in saturated cyclic or acyclic systems.[5-9] As an extension of these investigations, we report the synthesis of α,β-unsaturated 1,2-semidiones (**1**) and several of their benzo derivatives (**2**) in the five- and six-membered ring systems. The present results complement the previously reported analysis of the ketyls of α,β-unsaturated ketones (**3, 4**).[10]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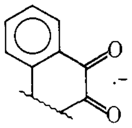
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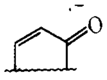
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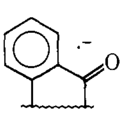
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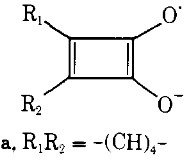
Results and Discussion

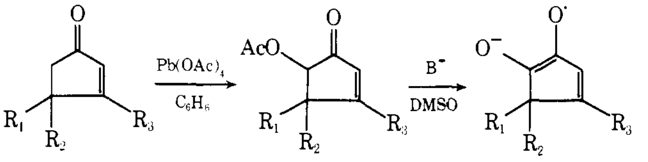
Although electroreduction of benzocyclobutenedione in acetonitrile produced the radical anion **5a**,[11] electroreduction of dimethylcyclobutenedione[12] or methylmethoxycyclobutenedione[13] in dimethoxyethane (−70 to +25°) failed to give esr spectra consistent with **5b** and **5c**. Attempts to generate **5b** and **5c** by reduction of the unsaturated diones with dimethyl sulfoxide (DMSO) solutions of potassium *tert*-butoxide[14] were also unsuccessful.



5a, R_1R_2 = -$(CH)_4$-
b, $R_1 = R_2 = CH_3$
c, $R_1 = CH_3$; $R_2 = CH_3O$

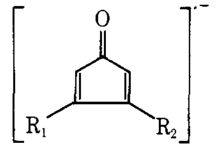
Treatment of 4,4-dimethyl-2-cyclopentenone with potassium *tert*-butoxide and oxygen in DMSO directly in the esr cavity[15] failed to produce the semidione **7a** in detectable amounts. However, the acetoxy ketone (**6a**, Scheme I) yielded the unstable radical anion **7a** when treated with base in DMSO. In a similar fashion the trimethyl derivative **7c** was produced. The presence of $R_3 = CH_3$ conferred considerable stability to **7** and **7c** could be easily observed in a static system over a period of several hours. When **6b** or **6d** was treated with potassium *tert*-butoxide-DMSO in a flow system, semidiones **7b and 7d** could not be detected; instead esr signals consistent with cyclopentadiene ketyls (**8**) were observed. Apparently **6b** and **d** underwent an elimination reaction to the cyclopentadienone in preference to hydrolysis to the hydroxy ketone.

Scheme I



6 7

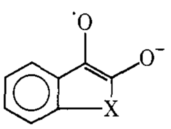
a, $R_1 = R_2 = CH_3$; $R_3 = H$
b, $R_1 = R_2 = H$; $R_3 = CH_3$
c, $R_1 = R_2 = R_3 = CH_3$
d, $R_1 = H$; $R_2 = R_3 = CH_3$



8a, $R_1 = R_2 = H$; $a^H = 5.3$ (2) 2.9 (2) G[14]
b, $R_1 = H$; $R_2 = CH_3$; $a_{CH_3}{}^H = 6.2$, $a^H = 5.3, 3.5, 2.4$ G
c, $R_1 = R_2 = CH_3$; $a_{CH_3}{}^H = 5.9$ (2), $a^H = 2.5$ (2) G

The esr spectrum of **7a** consisted of a doublet of doublets (a^H = 1.50 and 6.60 G) which was further split into a septet of 0.73 G. The 1.5 and 6.6 G couplings were assigned to the α- and β-hydrogens, respectively, by analogy to **8** and **10**. The observation of high spin density at the β-position (relative to the α-position) in acyclic α,β-unsaturated ketyls has also been reported.[10,16]

Interestingly, the benzo derivative of **7**, indan-1,2-semidione (**7B**, X = CH_2), is readily formed and has sufficient stability to be observed in aqueous solution.[17] The preparation of **7B** with X = C=O, S, O, NCH_3, $C(CH_3)_2$,



7B

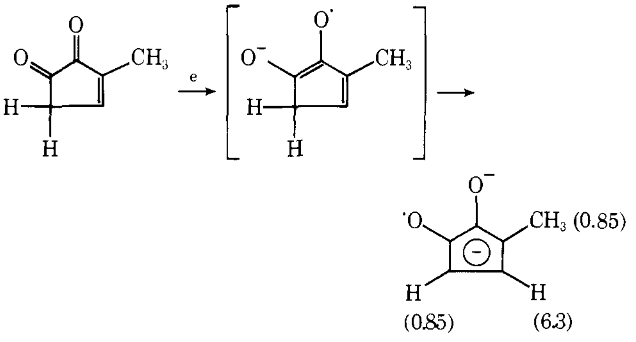
Table I. Hyperfine Splitting Constants (G) for **10** in DMSO at 30°

Derivative	Position H-3	H-4	H-5	H-6
b	1.57	5.27[a]	2.63, 4.83	7.95
c	1.57	5.32[a]	3.42, 3.42	0.15,[a] 0.15[a]
d	1.57[a]	5.42		5.63, 5.63
e	1.71	5.19		5.75, 5.75
f	1.69	4.84		5.28, 5.28

[a] $a_{CH_3}{}^{H}$.

$C(OCH_3)_2$, NH, N^-, and NO^- has also been reported.[17] These radical anions were also considerably more stable than **7**, reflecting the stabilization effect of the benzene ring.

Electrolytic reduction of 3-methylcyclopent-3-ene-1,2-dione[18] gave an esr signal with hfs by a^H = 6.3, 0.85 G and $a_{CH_3}{}^{H}$ = 0.85 G. We conclude that dissociation to give a radical dianion (**9**) possessing the aromatic sextet occurred.



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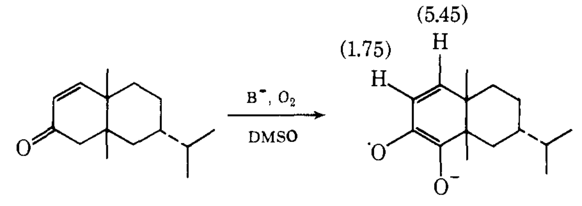
The conjugated unsaturated 1,2-semidiones in the six-membered ring (**10**) were also difficult to prepare with the exception of **10a**, which was produced from the octalone[19]



10a

by oxidation in basic DMSO solution. Similar treatment of the appropriate cyclohexenones failed to generate the 1,2-semidiones **10b–f** or formed the 1,4-semidiones. However, these 1,2-semidiones could be prepared from the acetoxy ketones by reaction with basic DMSO solution (Scheme II, Figure 1).

Semidiones **10b**, **c**, and **f** decayed slowly in DMSO solution at 30° as evidenced by their esr spectra. This behavior was strikingly contrasted by **10d** and **10e** which decayed rapidly under these conditions. The esr spectrum of **10d** could be recorded under static conditions whereas the spectrum of **10e** had to be recorded under flow conditions, since the lifetime of this radical was only several seconds at 30° in DMSO. The reaction of 6-acetoxy-2-cyclohexen-1-one or 6-acetoxy-5-methyl-2-cyclohexen-1-one with basic DMSO solution under flow conditions failed to give esr spectra consistent with their corresponding conjugated unsaturated semidiones even when the time between mixing and esr detection was 0.1 sec.

The hyperfine splitting constants (hfsc) obtained from the spectra of **10** and their assignments are given in Table I. The methyl substitutions in **10** clearly establish the higher spin density at C-4 relative to C-3.

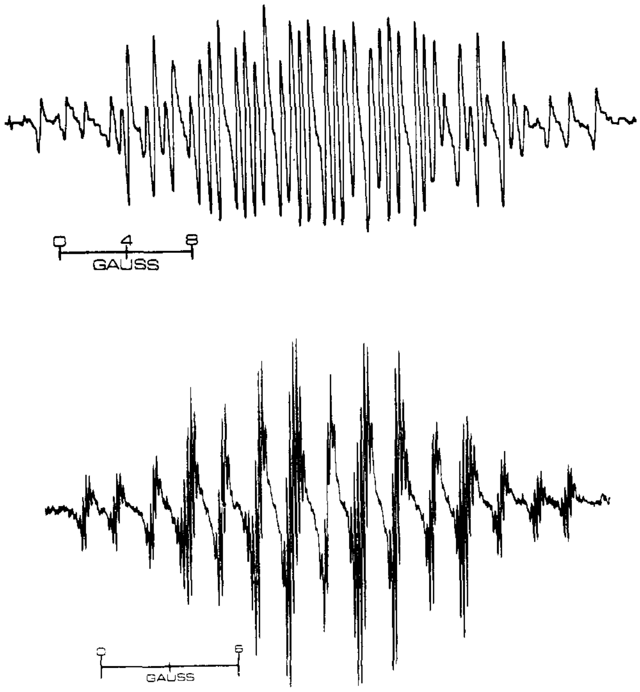
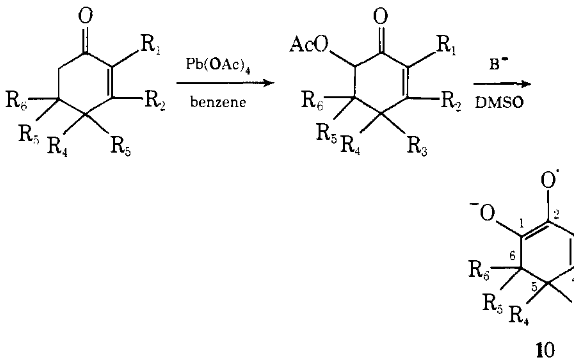


Figure 1. First-derivative esr spectra observed in DMSO for semidiones **10b** (top) and **10c** (bottom).

Scheme II

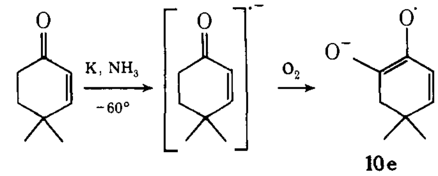


10

b, $R_2 = R_5 = CH_3$;
$R_1 = R_3 = R_4 = R_6 = H$
c, $R_2 = R_5 = R_6 = CH_3$;
$R_1 = R_3 = R_4 = H$
d, $R_1 = R_3 = R_4 = CH_3$;
$R_2 = R_5 = R_6 = H$
e, $R_3 = R_4 = CH_3$;
$R_1 = R_2 = R_5 = R_6 = H$
f, $R_3 = R_4 = C_6H_5$;
$R_1 = R_2 = R_5 = R_6 = H$

Bersohn and Chen have reported that the reduction of 4,4-dimethyl-2-cyclohexen-1-one with alkali metal in liquid ammonia yields the unsaturated ketyl.[20] However, the esr spectrum reported is identical with the one obtained from **10e**. Evidently, oxygen was present in their system resulting in the formation of the unsaturated semidione (Scheme III).

Scheme III



10e

The acetoxy ketones which either failed to give unsaturated semidiones or yielded very unstable ones produced

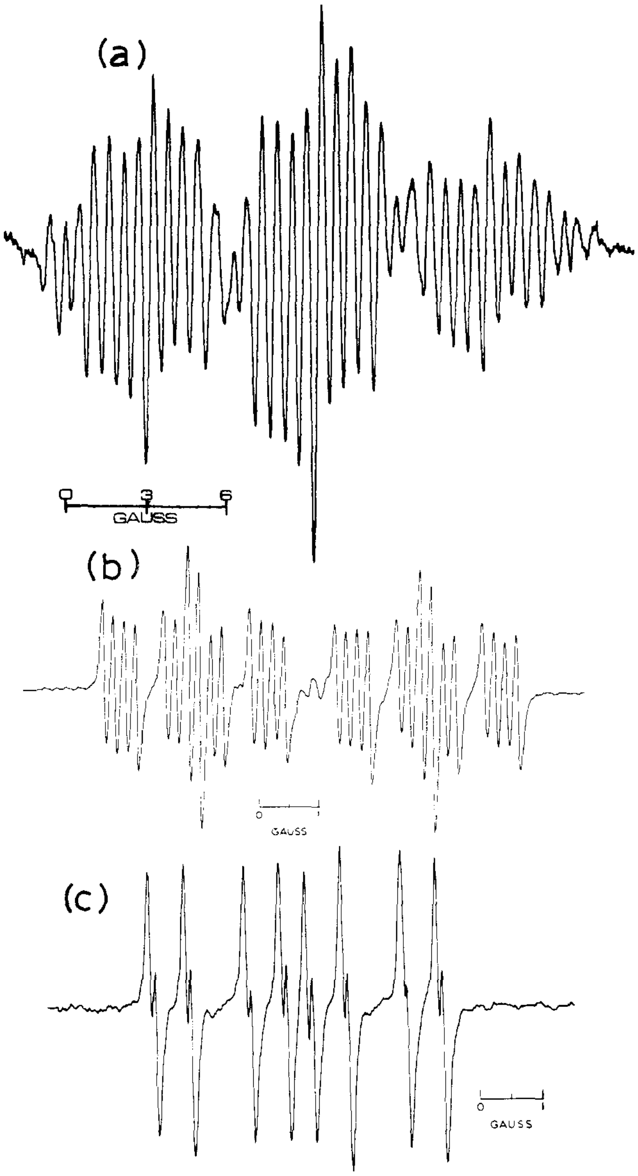
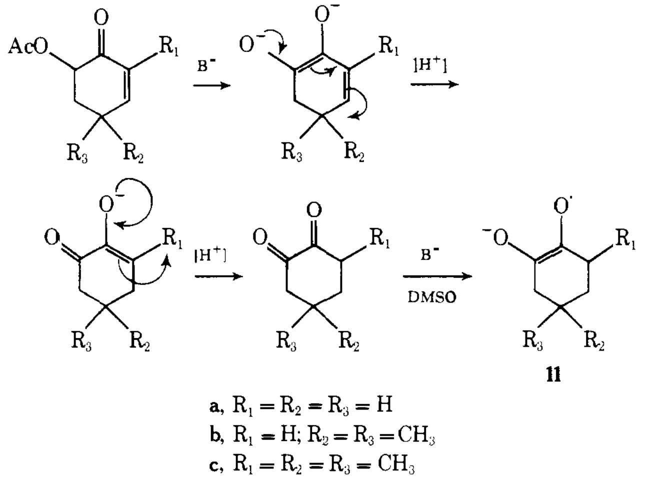


Figure 2. First-derivative esr spectra in DMSO of (a) semidione **12a**, (b) semidione **13h**, and (c) semidione **13g**.

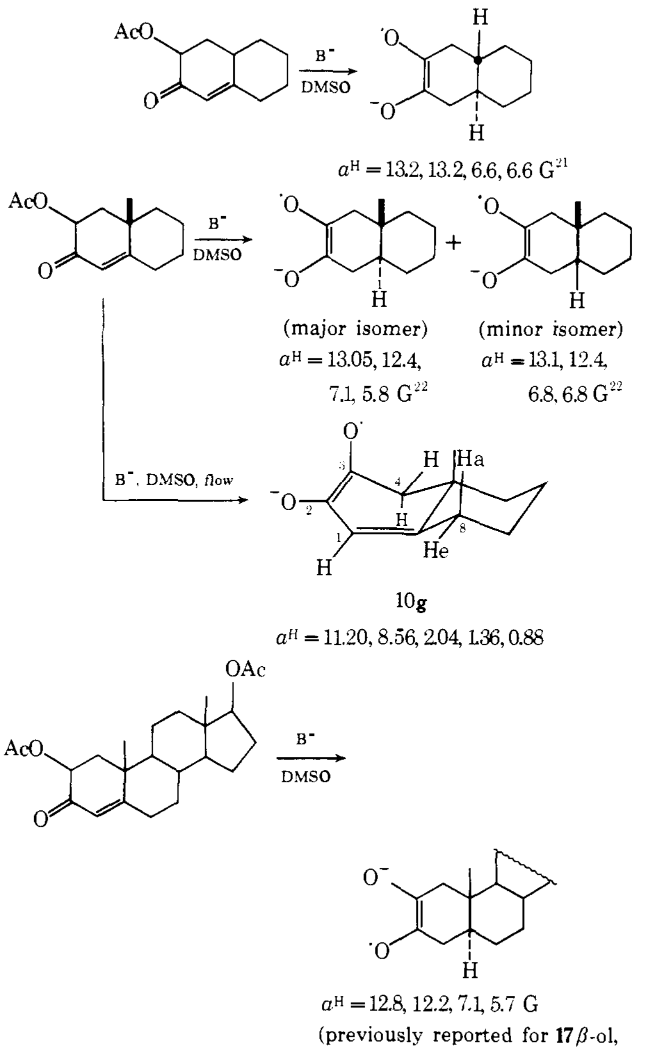
saturated semidiones upon treatment with excess potassium *tert*-butoxide in DMSO solution (Scheme IV). The esr spectra obtained from **11a** and **b** were identical with those previously reported.[15,21] The hfsc obtained from **11c** (a^H = 5.87, 11.00, and 12.70 G) are in excellent agreement with those reported for **11** with $R_1 = CH_3$; $R_2 = R_3 = H$ (a^H = 8.56, 10.29, and 11.15 G).[21] Interestingly, **10b–c** were stable in DMSO solutions of excess potassium *tert*-butoxide, and no spectral evidence for their corresponding saturated semidiones was observed. It is conceivable that the presence of a methyl group at C-4 in **10** hinders the protonation of the corresponding dianion (see Scheme IV) at that position. We have also observed the formation of saturated semidiones[22] from unsaturated acetoxy ketones in the octalin ring system with basic DMSO solutions (Scheme V). Under flow conditions $\Delta^{1,9}$-3-acetoxy-10-methyl-2-octalone gave a well-resolved esr spectrum assigned to **10g**. Under similar conditions the unsaturated semidione without the angular methyl group could not be identified. The assignment of hfsc for **10g** requires drastic magnetic nonequivalence of the hydrogen atom at C-4 and C-8. Models indicate that the axial carbon-hydrogen bond at C-8 is nearly parallel to the p_z orbital at C-9. The following assignment of hydrogen hfsc seems most reasonable; $a_{axC\text{-}8}$ = 11.20, $a_{axC\text{-}4}$ = 8.56, $a_{eqC\text{-}4}$ = 2.04, $a_{H\text{-}1}$ = 1.36, $a_{eqC\text{-}8}$ = 0.88 G.

Scheme IV



a, $R_1 = R_2 = R_3 = H$
b, $R_1 = H$; $R_2 = R_3 = CH_3$
c, $R_1 = R_2 = R_3 = CH_3$

Scheme V

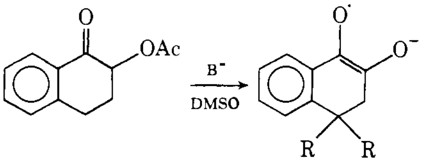


Attempts to prepare the benzo derivative of the α,β-unsaturated cyclohexane semidione (**12a**) from α-tetralone by oxidation in basic DMSO solution were unsuccessful. However, 2-acetoxy-1-tetralone spontaneously yielded **12a** upon treatment with deoxygenated basic DMSO solutions. The esr spectrum of **12a** (Figure 2a) is consistent with $a_{aromatic}{}^H$ = 2.23, 1.08, 0.65, and 0.40 G and $a_{CH_2}{}^H$ = 1.68 and 6.33

Table II. Hyperfine Splitting Constants (G) of **12** and **13** in DMSO at 30°

Semidione X–Y	$a_{\mathrm{aromatic}}^{\mathrm{H}}$	Other hfsc
12a	2.23, 1.08, 0.65, 0.40	$a_{\mathrm{CH_2}}^{\mathrm{H}} = 6.33, 1.68$
12b[23]	2.42, 2.42, 0.68, 0.68	$a_{\mathrm{CH_2}}^{\mathrm{H}} = 6.64$
13a	3.96, 2.47, 1.00, 0.49	$a_{\mathrm{CH}^-}^{\mathrm{H}} = 1.47$
13b	3.96, 2.47, 1.00, 0.49	$a_{\mathrm{CD}^-}^{\mathrm{H}} = 0.22$
13c	3.75, 2.70, 0.95, 0.75	$a^{\mathrm{N}} = 0.35$
13d	2.82, 1.91, 0.78, 0.35	$a^{\mathrm{N}} = 0.78$
13e	2.08, 2.08, 0.55, 0.55	$a_{\mathrm{CH_2}}^{\mathrm{H}} = 11.78$
13f	2.00, 2.00, 0.63, 0.63	$a_{\mathrm{CH_2}}^{\mathrm{H}} = 7.25$
13g	2.5, 1.5, 0.5, 0.1	
13h	1.45, 1.05, 0.4, <0.1	$a_{\mathrm{CH}}^{\mathrm{H}} = 3.95, 0.20$
13i[a]	1.45, 1.32, 0.55, 0.48	$a^{\mathrm{H}} = 0.66$, $a_{\mathrm{NH}}^{\mathrm{H}} = 0.08$
13j[b]	1.82, 1.59, 0.67, 0.61	$a^{\mathrm{N}} = 0.45$

[a] In DMSO (95%)–H_2O (5%). [b] In DMSO (80%)-*t*-BuOH (20%).

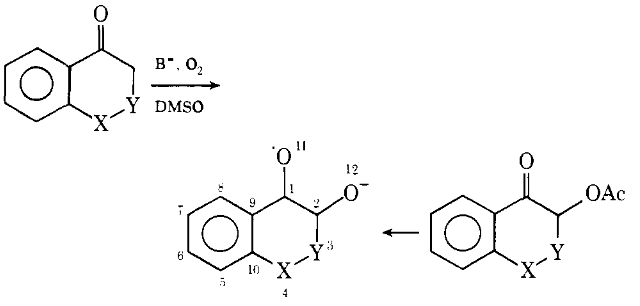


12a, R = H
b, R = CH_3

G. The 6.33 G coupling for the α-methylene hydrogens is in excellent agreement with the 6.64 G coupling reported for the analogous hydrogens in **12b**.[23]

A variety of heterocyclic analog of **12** (**13a–f**) were also prepared (Scheme VI). Oxidation of the ketones with X-Y = -SO_2CH_2-, -SO_2NH-, and -C(=O)NH- produced the paramagnetic derivative **13a, c,** and **d** in appreciable concentrations while with DMSO-d_6, base, and oxygen the precursor of **13a** yielded **13b**. Semidione **13d** was also prepared by treatment of 1,3,4-(2*H*)-isoquinolinetrione (phthalonimide) with a solution of base in DMSO. Oxidation of 4-chromanone and 4-thiochromanone in basic DMSO solution failed to give spectra consistent with **13e** and **13f**. However, reaction of the acetoxy derivatives with either basic DMSO solutions or basic methanolic solutions did produce **13e** and **13f** in low yields. Treatment of 2-oxo-3,4-dihydroxy-1,2-dihydroquinoline with base in DMSO produced the radical dianion (**10j**) or the radical anion (**10i**) depending on the concentration of base. Radical ions **10i** or **10j** were stable for a least 24 hr in the absence of oxygen and showed no tendency to decompose to isatin radical anion. However, in the presence of oxygen isatin radical anions[17] were formed, undoubtedly as a result of the benzilic acid rearrangement of 2,3,4-trioxo-1,2,3,4-tetrahydroquinoline (quinisatin, Scheme VII).[24]

Scheme VI



13

a, -X-Y- = -SO_2CH^--
b, -X-Y- = -SO_2CD^--
c, -X-Y- = -SO_2N^--
d, -X-Y- = -C(=O)N^--
e, -X-Y- = -OCH_2-
f, -X-Y- = -SCH_2-
g, -X-Y- = -C(O^-)=CH-
h, -X-Y- = -CH=CH-
i, -X-Y- = -NHCO-
j, -X-Y- = -N=C(O^-)-

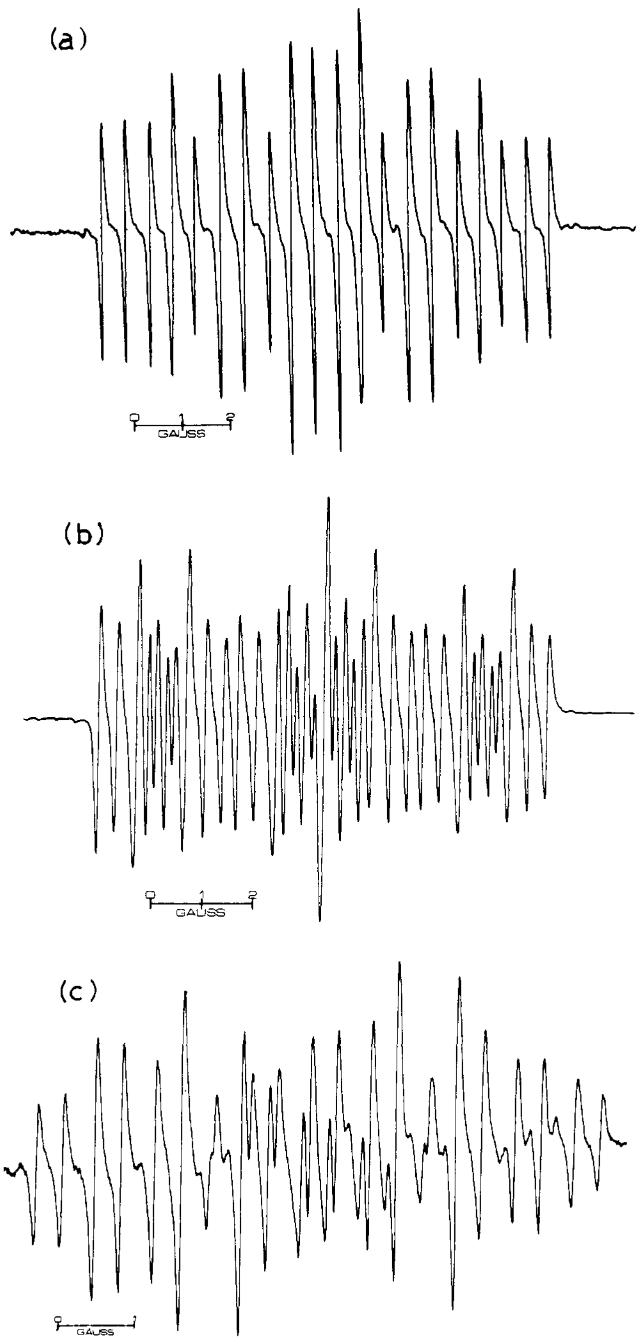
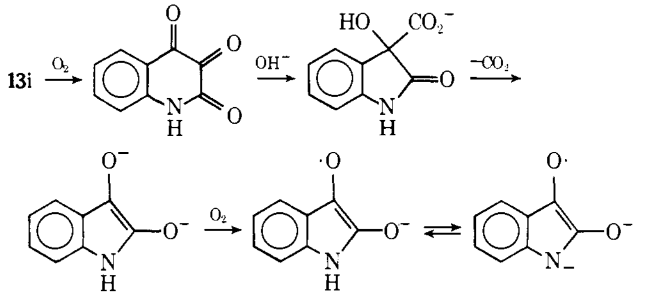


Figure 3. First-derivative esr spectra of heterocyclic semidione radical dianions (a) **13a**, (b) **13c**, and (c) **13d**.

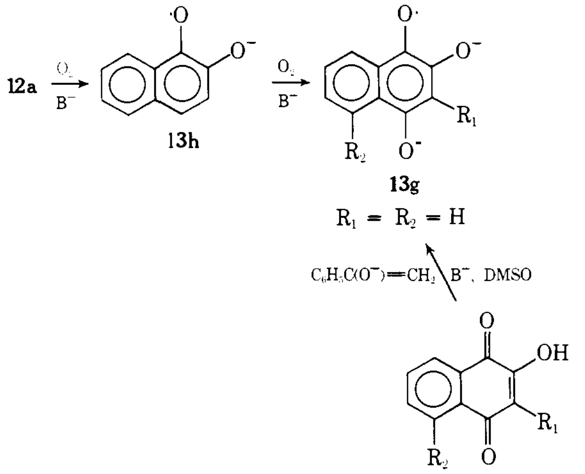
The hfsc's of **13a–f** are given in Table II and representative spectra are shown in Figure 3. The postulated loss of a proton from C-3 in **13a–d** to give radical dianions is based upon several observations. First, an observable hfsc for a hydrogen at the 3-position might be expected since the analogous hydrogen in isatin radical anion (**13**, X-Y = >NH) has a value of 0.19 G.[17] Secondly, the hydrogen atom at the 3-position in **13a** is readily exchanged in basic

Scheme VII



DMSO solution. Finally, the spin densities for **13d** calculated by the McLachlan MO method[25] are in agreement with the observed values (Table III). The tendency for **13a–d** to exist as radical dianions undoubtedly is a consequence of aromaticity. A sextet of electrons is achieved by dissociation of a proton from position 3. Surprisingly, the sulfone group appears able to participate in this aromatic cycle, presumably by use of d orbitals.

The aromatic radical dianion **13g** (Figure 2c) is a commonly encountered radical ion from ten carbon unsaturated ketonic precursors. It is the final and sometimes the only paramagnetic oxidation product observed when the following ketones are treated with oxygen in basic DMSO solution: *o*-naphthoquinone, *p*-naphthoquinone,[26] α- and β-tetralones, $\Delta^{1,9}$-3-acetoxy-2-octalone, $\Delta^{1,9}$-2-octalone, bullvalone, bicyclo[4.2.2]deca-2,4,7-trien-9-one, 4,5-benzocycloheptanone, 2,3-benzo-4-cycloheptenone, and 3,4-benzobicyclo[4.1.0]heptan-2-one. In some cases **12a** and/or **13h** (Figure 2b) could be detected as precursors to **13**.[27] The autoxidation of α- or β-tetralones,[28,29] 1-keto-1,2,3,4-tetrahydrophenanthrene,[29] and 1,2- or 1,3-dihydroxynaphthalenes[28] in basic solution to α-hydroxy-1,4-naphthaquinones or the corresponding phenanthrenequinone is well known, as well as the conversion of 2,5-dioxo-1,2,5,6,7,8-hexahydroquinoline to 6-hydroxy-5,8-dioxocarbostyril.[30] Although **13h** could be detected as an intermediate in the oxidation of α- or β-tetralone in basic solution, the reaction of basic DMSO with α-tetralyl hydroperoxide led first to the 1,4-naphthosemiquinone and then to **13g**. *tert*-Butyl hydroperoxide, base, and α-tetralone, on the other hand, yielded first the 1,2-naphthosemiquinone **13h** and then **13g**. The conversion of α-tetralyl hydroperoxide to the 1,4-semiquinone can be rationalized by Scheme VIII. On the other hand, the autoxidation of the ketones in basic solution appears to follow Scheme IX.



$R_1 = R_2 = H$

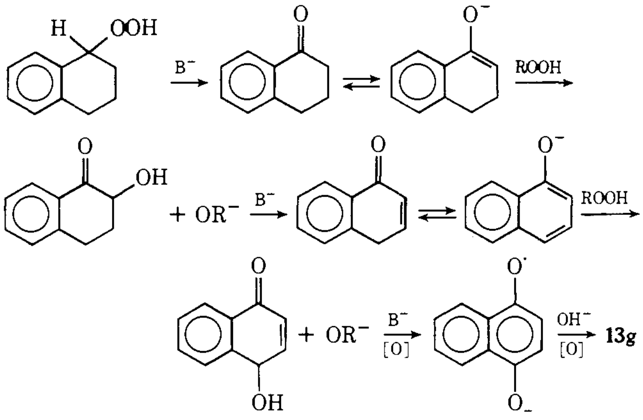
$R_1 = R_2 = H$, lawsone
$R_1 = CH_3$; $R_2 = H$, phthiocol
$R_1 = H$, $R_2 = OH$, juglone

Table III. HMO Computed McLachlan Spin Density for **13d**

Position	Calcd, ρ: *a*	Calcd, ρ: *b*	Exptl, ρ[c]
1	0.2396	0.4454	
2	0.1583	0.2376	
3	−0.0210 (0.006)[d]	−0.0007 (0.024)[d]	
4	0.1339	0.2671	
5	0.0156 (0.0306)[d]	0.0736 (0.067)[d]	0.033
6	0.0503 (0.0507)[d]	0.0972 (0.080)[d]	0.081
7	0.0157 (0.0273)[d]	−0.0124 (0.019)[d]	0.015
8	0.0515 (0.054)[d]	0.1700 (0.114)[d]	0.120
9	0.0101	0.0125	
10	0.0495	0.0218	
11	0.1335	−0.0959	
12	0.0865	−0.0888	
13[e]	0.0766	−0.0838	

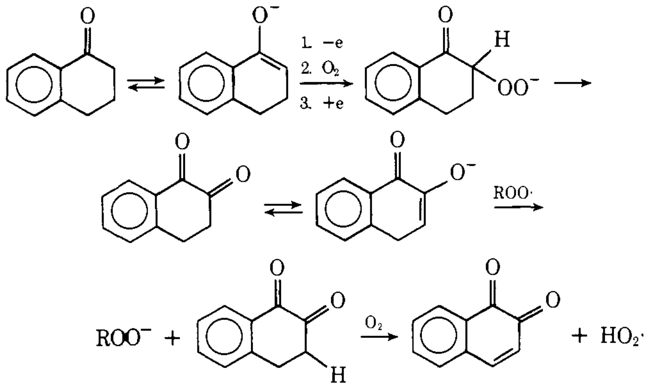
[a] $\beta_{C-O(13)} = 0.8$, $\beta_{CC} = \beta_{CN}$, $\beta_{C-O(11,12)} = 1.4$, $\alpha_{O(11,12)} = \alpha_C + 1.8\beta_{CC}$, $\alpha_{O(13)} = \alpha_C + \beta_{CC}$, $\alpha_N = \alpha_C + 1.5\beta_{CC}$. [b] $\beta_{CO} = \beta_{CN} = \beta_{CC}$, $\alpha_O = \alpha_C + 1.8\beta_{CC}$, $\alpha_N = \alpha_C + 1.5\beta_{CC}$. [c] $Q = -24$ G [d] Hückel spin densities. [e] Oxygen atom attached at C-4.

Scheme VIII

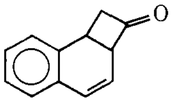


R = α-tetralyl

Scheme IX



The 12-carbon ketones **14–16** all yielded **13g** upon oxidation in basic solution. Ketone **14** gave only **13g** whereas **15** gave initially[31] an esr signal with a^H = 3.12, 2.70, 0.90, 0.78, 0.38 G which yielded **13g** upon further oxidation. Ketone **16** upon oxidation in basic solution gave first an unstable radical anion, a^H = 1.84 (4 H), 2.45, 2.63, which decayed to **13g** after a few minutes. Addition of more oxygen regenerated the unstable radical anion which again decayed to **13g**. The formation of **13g** from 11- or 12-carbon bicyclic



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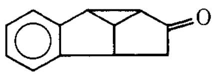

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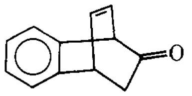

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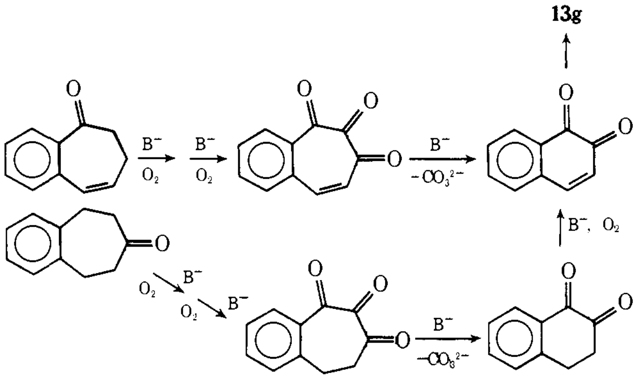
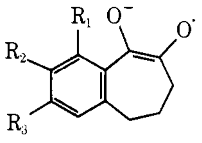
aromatic ketones can be explained by the oxidation to triones followed by benzylic acid rearrangements and decarboxylations (Scheme X).

Scheme X



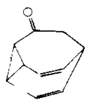
Radical ion **13g** was also formed when ethyl *o*-benzenedipropionate[32] was subjected to the acyloin condensation in dimethoxyethane (Na-K alloy) and the resulting crude product treated with base in DMSO.[33] A reasonable explanation is that the diester underwent the Dieckmann condensation followed by decarboxylation to 4,5-benzocycloheptenone.

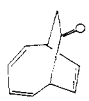
2,3-Benzocylohepten-1-one reacted with a trace of oxygen in basic DMSO solution to give radical anion **17a**. Apparently once this conjugated semidione in this seven-membered ring has been formed there is little driving force from additional conjugation to introduce a third carbonyl group. The complex esr splitting pattern indicates a nonplanar conformation for this cyclohepadiene derivative. Semidiones **17b** and **17c** were prepared by oxidation of 8,9,10-trimethoxy-2,3-benzocyclohepten-1-one[34] and 2,9,10-trimethoxy-8-hydroxy-6,7-benzocyclohepten-1-one.[34] The observed hfs patterns suggest that the 6.9 G splitting in **17a** is at the α-position and that the 2.5 G hfs is caused by the aromatic ortho hydrogen. 2-Cycloheptenone or 2-cyclooctenone failed to yield esr signals when oxidized in basic DMSO with the standard techniques.

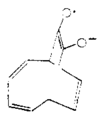


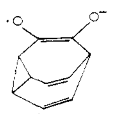
17a, $R_1 = R_2 = R_3 =$ H; $a^H = 6.9, 2.5, 0.75, 0.75, 0.3, 0.3, 0.15$ G
b, $R_1 = R_2 = R_3 = OCH_3$; $a^H = 0.3, 0.7, 0.7, 0.7$ G
c, $R_1 =$ OH; $R_2 = R_3 = OCH_3$; $a^H = 6.3$G,
all other $a^H < 0.5$ G

The conversion of bullvalone (**18**) and the isomeric ketone **19** to **13g** upon oxidation in basic solution has not been completely investigated. Treatment of **19** with traces of oxygen has occasionally yielded **20,** $a^H = 2.95$ (2), 1.3 (2), 0.33 (4) G. Excess oxygen readily converts **20** to **13g**. Semidione **20** can also be produced from the α-acetoxy derivative of **19** upon treatment with potassium *tert*-butoxide in DMSO. When generated from the acetoxy ketone in the absence of oxygen, the semidione **20** shows no tendency to rearrange and dehydrogenate to **13g**. Upon oxygenation of **20** obtained from the acetoxy ketone, **13g** can again be detected. One can imagine conversion of **20** and **21** to 9,10-dihydronaphthalene-1,2-semiquinone (**22**), which would be easily oxidized and hydroxylated to give **13g** in the presence of traces of oxygen (Scheme XI). The simplest rearrangement would be a 1,3-sigmatropic shift of the butadienyl bridge in **20** to give **22** directly although other mechanisms can be imagined including a 1,3-shift of the semidione bridge.[35] The thermolyses of bullvalene and bicyclo-[4.2.2]deca-2,4,7,9-tetraene to *cis*-9,10-dihydronaphthalene are well known.[36,37] The results accumulated to date seem to be best explained by an equilibrium between **20** and **22** in which **20** is highly favored.


18


19


2C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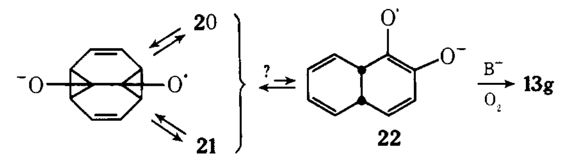
Scheme XI



The assignment of hfsc in **13g** was achieved by the synthesis of numerous derivatives. The assignment was somewhat complicated by the fact that the hfsc are solvent dependent. Table IV lists some of the more pertinent compounds studied as well as data for the corresponding *o*-naphthoquinones (**13h**), which were prepared by oxidation of the appropriate α-tetralone in basic DMSO solution.

Reduction of lawsone to its radical anion occurred in DMF or DMSO-potassium *tert*-butoxide containing propiophenone. The reducing ability of this solvent system with[41] or without[14] propiophenone enolate anion has been noted previously. The semiquinone was also observed upon treatment of lawsone with zinc in DMF (90%)-aqueous 30% potassium hydroxide (10%) or sodium dithionite in 0.1 *M* aqueous potassium hydroxide.[38]

Experimental Section

Esr Spectra. The preparation of radical ions by use of an inverted U-type mixing cell from α-hydroxy ketones or from the oxidation of monoketones in DMSO solution in the presence of potassium *tert*-butoxide has been previously reported.[31] In the flow experiments 250-500 ml of ~0.025 *M* deoxygenated (by a stream of prepurified nitrogen) solutions of the α-acetoxy ketone in DMSO were continuously mixed with an identical volume of ~0.050 *M* deoxygenated solutions of potassium *tert*-butoxide in DMSO in a Varian Associate V-4549A cell located in the cavity of the esr spectrometer. The cell had a volume of ~0.05 ml between the point of mixing and detection. The flow rate of the mixed solution was 13 ml/min. The electrolysis was done directly in the esr cavity using tetra-*n*-butylammonium perchlorate as the supporting electrolyte in a Varian flat fused silica electrolytic cell with mercury cathode and platinum anode. The emf across the electrodes was increased until a signal could be detected. Spectra were recorded either on a Varian Associates V-4500 or E-3 spectrometer. Spectra were simulated with a Japan Electron Optics Laboratory Co., JNM-RA-1 spectrum accumulator by the superposition of a series of Lorentzian line with widths of 0.1 G or less.

Preparation of α-Acetoxy Ketones. A mixture of the ketone and lead tetraacetate in a ratio of 1:1.1 in dry benzene (100 ml/0.05 mol of the ketone) was heated to reflux as described by Ellis.[42] After cooling the benzene solution was washed with water, saturated aqueous $NaHCO_3$, and saturated aqueous NaCl before drying over $MgSO_4$. Removal of the benzene under reduced pressure left a mixture of the acetoxy ketone and unreacted starting material. The crude acetoxy ketone from 5,5-dimethylcyclopent-2-enone[43] was used without isolation. **5-Acetoxy-3-methyl-2-cyclopenten-1-one** was prepared by lead tetraacetate oxidation of 3-methyl-2-cyclopentene-1-one and was purified by elution from a silica gel column (ethyl acetate-hexane): ir (neat) 1751, 1718 (C=O) 1620 (C=C), 1234 cm^{-1} (C—O—C); pmr (CCl_4) δ 2.05 (s, 3), 2.14 (s, 3), 2.45-3.25 (m, 2), 4.99 (q, 1, $J = 7.1$ and 3.5 Hz), 5.88 (broad s, 1); mass spectrum (70 eV) *m/e* (rel intensity) 154 (1), 112 (6), 111 (5), 96 (10), 95 (3), 94 (4).

Table IV. Hyperfine Splitting Constants Observed for Derivatives of **13g** and **13h**

Substituent	Solvent	a^H (G) H-3	H-4	H-5	H-6	H-7	H-8
13g, none[a]	DMSO	<0.1		0.5	2.5	0.1	1.5
13g, none[b]	*t*-BuOH (80%) H_2O (20%)	0.1		0.25	1.90	0.15	1.50
13g, none[b]	H_2O[c]	0.1 (?)		0.28 (?)	1.87	0.1	1.48
13g, 3-deuterio[d]	DMSO-d_6			0.5	2.5	0.1	1.5
13h, none[e]	DMSO	0.2	3.95	<0.1	1.45	0.40	1.05
13h, 4-CH_3[e]	DMSO	0.2	4.00[f]	<0.1	1.40	0.34	1.05
13g, 3-CH_3[b,g]	DMSO	0.40[f]		0.55	2.50	0.08	1.45
13g, 3-CH_3[b,g]	H_2O[c]	0.38[f]		0.26	2.98	0.13	1.51
13g, 3-CH_3O[b,h]	H_2O			0.20	1.80		1.50
13g, 5-CH_3[b,e]	DMSO				2.50	0.30	1.40
13g, 3-deuterio-5-hydroxy[i,j]	DMF-D_2O				2.58	0.51	2.17
13h, 5-CH_3O[e]	DMSO	0.18	4.00		1.45	0.50	0.98
13h, 6-CH_3O[e]	DMSO	0.26	4.20	<0.1	0.13[b]	0.40	1.08
13g, 6-CH_3O[e]	DMSO			0.45	0.15[b]	0.30	1.30
13g, 7-CH_3O[e]	DMSO			0.6	2.30		1.85
13h, 7-CH_3O[e]	DMSO	0.10	3.90	<0.1	1.40		1.20

[a] From *o*-naphthoquinone, lawsone, and α- or β-tetralone. [b] From lawsone or the substituted lawsone. [c] Reference 38. [d] From 4.5-benzosuberone-d_6. [e] From the α-tetralone. [f] $a_{CH_3}{}^H$. [g] From phthiocol. [h] Reference 39. [i] From juglone. Reference 40. [j] $a_{CH_3O}{}^H$.

Anal. Calcd for $C_8H_{10}O_3$: C, 62.31; H, 6.54. Found: C, 62.36; H, 6.86.

5-Acetoxy-3,4-dimethyl-2-cyclopenten-1-one was prepared from 3,4-dimethyl-2-cyclopenten-1-one[44] and was purified by elution from a silica gel column (ethyl acetate-hexane). This gave a 1:2 cis-trans mixture: ir (neat) 1750, 1722 (C=O), 1620 (C=C), 1242 cm^{-1} (C—O—C); pmr ($CHCl_3$) trans δ 1.35 (d, 3, *J* = 8.0 Hz), 2.13 (s, 3), 2.16 (s, 3), 2.41-3.22 (m, 1), 4.78 (d, 1, *J* = 3.2 Hz), 5.95 (broad s, 1); cis δ 1.05 (d, 3, *J* = 8.0 Hz), 2.13 (s, 3), 2.16 (s, 3), 2.41-3.22 (m, 1), 5.25 (d, 1, *J* = 7.1 Hz), 5.95 (broad s, 1); mass spectrum (70 eV) *m/e* (rel intensity) 168 (1), 126 (12), 111 (17), 108 (16).

Anal. Calcd for $C_9H_{12}O_3$: C, 64.25; H, 7.20. Found: C, 64.23; H, 7.21.

5-Acetoxy-3,4,4-trimethyl-2-cyclopenten-1-one was prepared from 3,4,4-trimethyl-2-cyclopenten-1-one[44] and was purified by elution from a silica gel column (ethyl acetate-hexane): ir (neat) 1750, 1719 (C=O), 1614 (C=C), 1235 cm^{-1} (C—O—C); pmr (CCl_4) δ 1.09 (s, 3), 1.32 (s, 3), 2.10 (s, 3), 2.20 (s, 3), 5.10 (s, 1), 5.90 (broad s, 1); mass spectrum (70 eV) *m/e* (rel intensity) 182 (1), 140 (5), 125 (17), 111 (2), 109 (1).

Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.89; H, 7.75. Found: C, 65.62; H, 7.96.

3,5-Dimethyl-2-cyclohexen-1-one yielded a mixture of *cis-* and *trans*-**6-acetoxy-3,5-dimethyl-2-cyclohexen-1-one** purified by glpc (10% QF-1) at 180°: ir (neat) 1731 and 1675 (C=O), 1622 (C=C) 1224 cm^{-1} (C—O—C); pmr (CCl_4) δ 0.88-1.15 (q, 3), 1.94 (s, 3), 2.09 (s, 3), 2.11-2.73 (m, 3), 5.07 (2 doublets, 1; *J* = 4.7 and 12.5 Hz), 5.70 (broad s, 1); mass spectrum (70 eV) *m/e* (rel intensity) 182 (1), 140 (5), 122 (105).

Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found: C, 66.13; H, 7.94.

6-Acetoxy-3,5,5-trimethyl-2-cyclohexen-1-one was prepared from isophorone, mp 74-75° (lit.[34] mp 76-78°).

6-Acetoxy-2,4,4-trimethyl-2-cyclohex-1-one was prepared from 2,4,4-trimethyl-2-cyclohexen-1-one and purified by glpc (10% QF-1 at 170°) to give a product with mp 46-47°: ir (neat) 1750 and 1688 (C=O), 1638(C=C), 1235 cm^{-1} (C—O—C); pmr (CCl_4) δ 1.16 (s, 3), 1.27 (s, 3), 1.71 (d, 3, *J* = 1.5 Hz), 1.76-1.97 (m, 2) 2.07 (s, 3), 5.37 (t, 1, *J* = 10 Hz), 6.36 (broad s, 1); mass spectrum (70 eV) *m/e* (rel intensity) 196 (1), 154 (3), 136 (11).

Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found; C, 67.24; H, 8.49.

6-Acetoxy-4,4-diphenyl-2-cyclohexen-1-one was purified by silica gel chromatography with elution by hexane (75%)-methylene chloride (25%) to give mateial with the following characteristics: mp 105-107° (30% yield); ir (KBr) 1740 and 1681 (C=O) 1220 cm^{-1} (C—O—C); pmr (CCl_4) δ 2.07 (s, 3), 3.09-2.60 (m, 2), 536 (q, 1, *J* = 6.0 and 12.5 Hz) 6.22 (d, 1, *J* = 10 Hz), 7.29 (broad s, 6) 7.47 (broad s, 5) mass spectrum (70 eV) *m/e* (rel intensity) 306 (1), 264 (3), 246 (33), 220 (13), 218 (15).

Anal. Calcd for $C_{20}H_{18}O_3$: C, 78,41; H, 5.92. Found: C, 78.62; H, 5.97.

***cis-* and *trans*-6-Acetoxy-5-methyl-2-cyclohexen-1-one** was isolated by distillation at 65-67° (0.1 Torr) and further purified by glpc (10% QF-1 at 170°): ir (neat) 1748 and 1690 (C=O), 1613 (C=C), 1233 cm^{-1} (C—O—C); pmr CCl_4) δ 0.89-1.17 (q, 3), 2.11 (s, 3), 2.14-2.78 (m, 3), 4.82-5.42 (2 doublets, 1, *J* = 4.3 and 12.5 Hz); 5.9 (q, 1), 7.06-6.61 (m, 1); mass spectrum (70 eV) *m/e* (rel intensity) 168 (1), 126 (13), 108 (44), 68 (100).

Anal. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 64.54; H, 7.40.

6-Acetoxy-2-cyclohexen-1-one was isolated by distillation, bp 82-83° (2.5 Torr) in 40% yield: ir (neat) 1732 and 1677 (C=O), 1608 (C=C) and 1232 cm^{-1} (C—O—C); pmr (CCl_4) δ 2.07 (s, 3); 1.81-2.77 (m, 4), 5.20 (q, 1, *J* = 6.6 and 12.0 Hz), 5.80-6.08 (m, 1), 6.75-7.11 (m, 1); mass spectrum (70 eV) *m/e* (rel intensity) 154 (1), 112 (7), 94 (5).

Anal. Calcd for $C_8H_{10}O_3$: C, 62.33; H, 6.54. Found: C, 62.08; H, 6.73.

2-Acetoxy-3,4-dihydro-1(2*H*)-naphthalenone was isolated by distillation of the unreacted α-tetralone (90-100° at 0.05 Torr) and crystallized from ether at −78°: mp 77-79° (lit.[45] mp 72-73°); pmr (CCl_4) δ 2.1 (s, 3), 2.12-2.43 (m, 2), 2.93-3.32 (m, 2), 5.37 (q, 1, *J* = 7.0 and 11.0 Hz), 7.03-7.57 (m, 3), 7.82-8.06 (m, 1).

3-Acetoxy-4-chromanone was crystallized from hexane: mp 80-81° (lit.[46] mp 74°); pmr (CCl_4) δ 2.18 (s, 3), 4.28-4.63 (m, 2), 5.62 (q, 1, *J* = 6.1 and 11 Hz), 6.87-8.00 (m, 4). **3-Acetoxy-4-thiochromanone** was purified by chromatography on silica gel with elution by hexane (75%)-methylene chloride (25%) to give material with the following characteristics: mp 78-80°; ir (KBr) 1740 and 1690 (C=O), 1232 cm^{-1} (C—O—C); pmr ($CDCl_3$) δ 2.14 (s, 3), 2.84-3.77 (m, 2); 5.61 (q, 1, *J* = 5.0 and 13.0 Hz), 6.92-7.50 (m, 3), 7.89-8.12 (m, 1); mass spectrum (70 eV) *m/e* (rel intensity) 222 (24), 180 (1), 162 (84), 135 (105).

Anal. Calcd for $C_{11}H_{10}SO_3$: C, 59.44; H, 4.54. Found: C, 59.71; H, 4.70.

$\Delta^{1,9}$-3-Acetoxy-2-octalone was prepared by the reaction of lead tetraacetate with $\Delta^{1,9}$-2-octalone[47] for 60 hr in refluxing benzene. Chromatography on silica gel and elution with hexane (85%)-ethyl acetate (15%) gave a viscous liquid crystallized from hexane to give material with the following characteristics: mp 91-95° in 15% yield; ir (KBr) 1739 and 1677 (C=O), 1630 (C=C), 1220 cm^{-1} (C—O—C); pmr (CCl_4) δ 1.06 (s, 3) 1.15-2.7 (m, 11), 2.06 (s, 3), 5.17 (q, 1, *J* = 5.7 and 13.8 Hz), 5.70 (broad s, 1); mass spectrum (70 eV) *m/e* (rel intensity) 208 (1), 166 (1), 148 (13), 122 (31).

Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 68.99; H, 7.78.

$\Delta^{1,9}$-3-Acetoxy-10-methyl-2-octalone was prepared from $\Delta^{1,9}$-10-methyl-2-octalone[48] by reaction with lead tetraacetate for 72 hr. Chromatography of the reaction product on silica gel and elution with hexane (80%)-ether (20%) gave a mixture of cis and trans isomers (34%) from which one isomer could be isolated in ~95% purity (16% yield) by crystallization from hexane: mp 100-102°; ir (KBr) 1740 and 1678 (C═O), 1618 (C═C), 1227 cm^{-1} (C—O—C); pmr (CCl_4) δ 1.38 (s, 3), 2.07 (s, 3) 1.42-2.5 (m, 10), 5.31 (q, 1, J = 8.5 and 11.0 Hz), 5.58 (broad s, 1); mass spectrum (70 eV) *m/e* (rel intensity) 222 (1), 180 (3), 162 (3), 136 (45).

Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.41; H, 8.30.

On exposure of the cis-trans mixture of isomers of $\Delta^{1,9}$-10-methyl-3-acetoxy-2-octalone to basic DMSO in the flow system, a radical anion with a^{H} = 11.20, 8.56, 2.04, 1.26, and 0.88 G was routinely observed. It appears that this unstable radical is the $\Delta^{1,9}$-2,3-semidione with $a_{ax}{}^{H}$ at C-4 and C-8 = 8.56 and 11.20 G, $a_{eq}{}^{H}$ at C-4 and C-8 = 2.04 and 0.88 G, and a^{H} at C-1 = 1.36 G. Upon stopped flow this radical was replaced by a mixture of *cis*- and *trans*-9-methyldecalin-2,3-semidione.

6-Acetoxy-4,4-dimethyl-2-cyclohexen-1-one was prepared according to the literature:[49] pmr (CCl_4) δ 1.22 (s, 3), 1.33 (s, 3), 1.9-2.6 (m, 2), 2.11 (s, 3), 5.45 (q, 1, J = 9.0 and 11.0 Hz), 5.87 (d, 1, J = 10.2 Hz), 6.71 (d, 1, J = 10.2 Hz).

Precursors for Benzoheterocyclic Semidiones. 2*H*-1,2-Benzothiazin-4(3*H*)-one 1,1-dioxide was synthesized from phenacylsaccharin,[50] mp 157-158° (lit.[50] 157-158°). **1,2,3,4-Tetrahydroisoquinoline-1,4-dione** was prepared from ethyl phthalimidoacetate,[51] mass spectrum (20 eV) *m/e* parent ion at 161.

Phthalonimide was prepared from 1,2,3,4-tetrahydroisoquinoline,[52] mp 225-226° (lit.[52] mp 224°).

2-Oxo-3,4-dihydroxy-1,2-dihydroquinoline (quinoline triol, precursor to **13i,j**) was prepared,[53] mp 288° (lit.[53] mp >300°). The melting point and ir spectrum did not change during three recrystallizations from ethanol: ir (KBr) 3300, 1610, 1590, 940, 755, 720, 670 cm^{-1}; mass spectrum (70 eV) *m/e* 177 (parent ion).

Anal. Calcd for $C_9H_7NO_3$: C, 61.01; H, 3.98; N, 7.91. Found: C, 61.0; H, 4.05; N, 7.81.

Benzocycloheptanone Derivatives. 2,3-Benzo-4-cycloheptenone was prepared from 3,4-benzobicyclo[4.1.0]heptan-2-one[54] by addition of 0.5 g of the tricyclic ketone to 8 g of potassium *tert*-butoxide (slurry) in 100 ml of benzene under nitrogen. After 2.5 min at reflux, the mixture was neutralized to pH 6 with dilute acid. The benzene layer was washed with 5% aqueous NaOH until the aqueous layer remained colorless. The benzene solution was then washed with saturated aqueous NaCl and distilled to give 0.3 g (60%) of material: bp 80-83° (0.22 Torr); pmr (CCl_4) δ 2.3-3.0 (m, 4), 5.9-6.6 (m, 2), 7.0-7.4 (m, 4); ir 1665 cm^{-1}. Reduction of 2,3-benzo-4-cycloheptenone with palladium on charcoal in ethanol at 1 atom of hydrogen for 24 hr yielded **2,3-benzocycloheptanone,** purified by glpc (15% Carbowax 20 M, 190°).

4,5-Benzocycloheptanone was prepared from diethyl 4,5-benzocycloheptadiene-2,7-dicarboxylate[55] by reduction to 4,5-benzocycloheptanone-2,7-dicarboxylic ester, bp 57-58°, followed by hydrolysis and decarboxylation. The reduced ester (3 g) was refluxed for 4 hr in 60 ml of 10% aqueous NaOH before acidificated to the Congo Red end point with dilute hydrochloric acid. The aqueous solution was stirred for 30 min at 30° and 30 min on a steam bath before being extracted with four portions of 20 ml of ether. The ethereal extracts were washed with water and 5% aqueous $NaHCO_3$ and dried over $MgSO_4$. Evaporation of the solvent gave 0.8 g of product: mp 41-42°; ir ($CHCl_3$), 1680 (C═O), 1550 (C═C), 1040, 985 cm^{-1}; pmr (CCl_4) δ 2.3-3.0 (m, 8), 7.1 (s, 4). Treatment of 200 mg of 4,5-benzocycloheptanone with 5 ml of deuteriomethanol containing a trace of sodium methoxide gave 4,5-benzocycloheptane-d_4 of 90% purity by pmr.

3,4-Benzobicyclo[4.1.0]heptan-2-one was prepared by treatment of 3-hydroxymethyl-α-tetralone with ethanolic sodium hydroxide[54] to give a product extracted with ether in 25% yield: bp 123° (1.0 Torr); ir 2820, 1665, 1010; pmr (CCl_4) δ 0.6-1.7 (m, 2), 1.8-2.2 (m, 2), 3.2 (d, 2), 7.0-7.6 (m, 4).

Diethyl *o*-benzenedipropionate was prepared from the condensation of monochloromalonic ester with α,α'-*o*-xylene dibromide.[32] Treatment of the reaction product with ethanolic KOH gave the diarylic acid which could be hydrogenated in saturated aqueous $NaHCO_3$ by Pd on charcoal to yield the saturated acid. Esterfication with ethanol and a trace of *p*-toluenesulfonic acid yielded a product which was extracted with saturated aqueous $NaHCO_3$ and aqueous NaCl and dried over Na_2SO_4, before the ethanol was removed by evaporation: pmr (CCl_4) δ 1.2 (t, 6), 2.35-3.0 (m, 8), 4.1 (q, 4), 7.1 (s, 4).

Tetralone and Lawsone Derivatives. α- and β-tetralone, 5-methoxytetralone, 6-methoxytetralone, 4-methyl-1-tetralone, lawsone, and juglone obtained from Aldrich Chemical Co. and phthiocol (K and K Laboratories) were used. Synthetic juglone[56] (mp 159-161°; pmr δ 6.88 (s, 2), 7.24 (m, 1), 7.55 (m, 2), 11.75 (s, 1)) gave the same esr spectrum as commercial material. This spectrum was unsymmetrical and contained approximately 58 lines. Apparently some type of base-catalyzed condensation had occurred. 5-Methoxytetralone (1 g) was converted to 5-methoxylawsone by reaction with 2 g of *p*-nitroso-*N*,*N*-dimethylaniline in 50 ml of ethanol containing 1 ml of 10% aqueous NaOH. After 2 hr a solid, 167-168° dec, was isolated which was hydrolyzed in 50 ml of 5% sulfuric acid.

7-Methoxytetralone[57] was prepared by cyclization of γ-(*p*-anisyl)butyric acid to yield material with the following characteristics: mp 59-60° (lit.[57] mp 61.0-62.5°); ir ($CHCl_3$) 1660, 1600 cm^{-}; pmr (CCl_4) δ 2.15 (m, 2), 2.4 (m, 2), 2.8 (t, 2), 3.75 (s, 3), 6.92 (m, 2), 7.35 (m, 1).

Bullvalone.[58] Ethyl cycloheptatriene-7-carboxylate (bp 60-64° at 2-4 Torr) was hydrolyzed to the free acid (bp 90-95°, 0.2 Torr), which upon treatment with thionyl chloride and a trace of pyridine in ether yielded the acid chloride, bp 55-60° (0.8 Torr).[59] The acid chloride (14 g) in 100 ml of ether was added dropwise to diazomethane (from 100 g of "Diazol") in 600 ml of ether and allowed to stand at 0° for 16 hr. The ether was evaporated, and the crude cycloheptatrienyldiazomethyl ketone in a mixture of benzene (80 ml) and hexane (60 ml) was added dropwise to a refluxing solution of 16 g of cupric sulfate in 160 ml of hexane under nitrogen. The mixture was refluxed for 1 hr before filtration. Distillation followed by steam distillation of the residue gave 4.8 of an ether-soluble oil which was dried over $MgSO_4$ and chromatographed on a 50 × 2 cm silica gel column using hexane-ether mixtures to yield 250 mg of barbaralone, mp 45-48° after sublimation (lit.[59] mp 40-48° after sublimation, 53.5° recrystallized from water). To a solution of 165 mg of barbarlone in 3.0 ml of methanol was added an ethereal solution of diazomethane (from 2 g of "Diazol"). After 30 hr at 0° the ether was evaporated and the residue chromatographed on silica gel with elution by hexane-ether mixtures to give 9-aldehydotricyclo[3.3.1.0^{4,6}]nona-2,7-diene and 100 mg of bullvalone, mp 36-37° (lit.[58] mp 36-37°).

Bicyclo[4.2.2]deca-2,4,9-trien-7-one (20) was prepared according to the literature procedure[60] from bicyclo[4.2.1]nona-2,4,7-trien-9-one[59] and diazomethane in 38%, bp 100-102° (5 Torr). The pmr and ir spectra were in agreement with the literature values. Ketone **20** (1.46 g) was converted to **8-acetoxybicyclo[4.2.2]deca-2,4,9-trien-7-one** by reaction with lead tetraacetate (4.9 g) in refluxing benzene (20 ml) for 72 hr. The reaction mixture was filtered through Celite, washed with saturated aqueous sodium bicarbonate and dried over sodium sulfate. Glpc analysis of the crude product indicated a 50:1 ratio of products, possibly syn and anti isomers. Evaporation of the benzene and recrystallization from 95% aqueous ethanol gave 0.75 g (37%) of material: mp 83.6-84.0°; pmr (CCl_4) δ 2.03 (s, 3 H), 3.2-3.8 (m, 2), ~5.3 (m, 1), 5.5-6.2 (m, 6); ir (KBr) 3030, 2930, 1735-1745, 1375, 1235 cm^{-1}; mass spectrum (70 eV) *m/e* 204 (parent), 134 (base).

The preparations of **benzobicyclo[2.2.2]octadiendienone (16)**, **4,5-benzobicyclo[4.2.0]octa-2,4-dien-8-one (14)** and **benzotricyclo[3.3.0.0^{2,8}]octen-3-one (15)** have been described.[61]

Acknowledgment. We thank Professor Chapman for samples of 8,9,10-trimethoxy-2,3-benzocyclohepten-1-one and 2,9,10-trimethoxy-8-hydroxy-6,7-benzocyclohepten-1-one.[34]

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(4) National Aeronautics and Space Administration Predoctoral Fellow, 1965–1968; Petroleum Research Fund Fellow, 1968–1969.

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Synthesis and Properties of Cycloocta[*def*]biphenylene, a Stable Benzenoid Paratropic Hydrocarbon[1,2]

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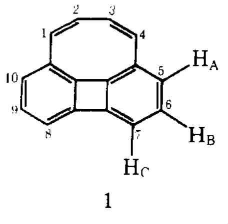
Received October 15, 1974

Abstract: The synthesis and properties of cycloocta[*def*]biphenylene are described. This hydrocarbon is predicted by conventional models to have simultaneously olefinic, aromatic, and antiaromatic properties. Experiments confirm these predictions. The resolution of this apparent contradiction is discussed.

Aromaticity has played a central role in the development of the theory of chemical bonding.[3] The archetypal extremes of behavior, benzene and cyclobutadiene, are now both known.[4] The elegant studies of the annulenes[5] and related ring structures[6] have highlighted the differences between $4n$ and $4n + 2$ ring systems.

The theory of aromaticity has been developed to the point where the chemical and physical properties of new π structures can be predicted with fair confidence.[3] An important concept that has emerged from the theoretical investigations is the trilogy of aromatic, olefinic, and antiaromatic classes;[7] much of the current interest in π systems is with molecules that lie on or near the borders of this classification scheme. This paper, describing in more detail results we have presented earlier,[1] is concerned with the particular molecule cycloocta[*def*]biphenylene (**1**) which according to the present classification criteria has the intriguing property of falling simultaneously into all three categories. This paper describes the synthesis of **1**, its chemical and physical properties, and concludes with a discussion of the limitations of the current classification methods.



1

According to simple HMO theory, molecules containing fused $4n$ rings are predicted[8] to have substantial delocalization energy and naively might have been expected to possess