1973

Unsaturated 1,4-semidiones

John Robert Mattox
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Unsaturated 1,4-semidiones

by

John Robert Mattox

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Department: Chemistry
Major: Organic Chemistry

Approved:

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Iowa State University
Ames, Iowa

1973

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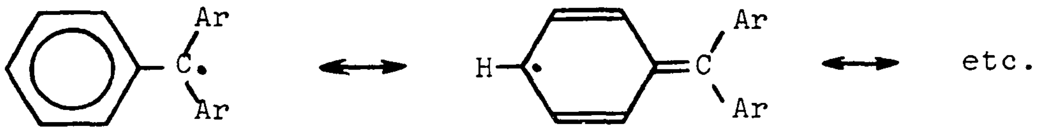
INTRODUCTION

ESR

Electron spin resonance spectroscopy is a powerful tool in organic chemistry for studying odd electron systems, either as transient reaction intermediates, or as stable entities. Under certain conditions, radical intermediates can be observed directly or, alternatively, by use of a spin trap, a molecule with appropriate functionality which can couple with the radical intermediate forming a stable spin adduct. The ESR spectra of these spin adducts are generally characteristic of the spin trap portion of the coupled product and give little direct information of the structure of the radical intermediate (1).

Structural information can be elucidated by the introduction of a spin label into a diamagnetic molecule. The resulting radical can be either neutral or charged. Experimentally, spin labels are most useful if they can be generated by an unambiguous route and have sufficient stability to allow observation at a steady state concentration, *ca*. 10^{-3}-10^{-6} M. Stability of neutral radicals may be achieved by extensive delocalization of the neutral center, as in the case of triarylmethyl radicals (**1**) or phenoxyl radicals (**2**).



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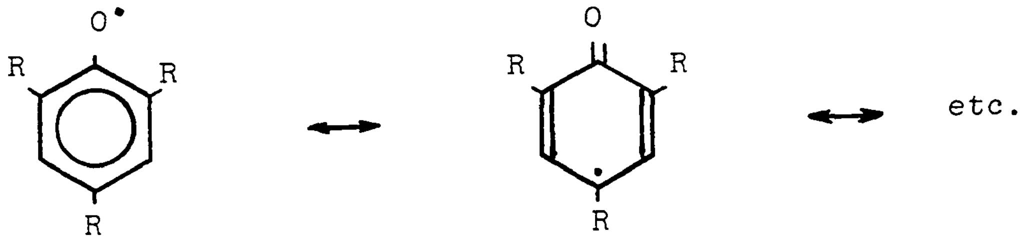

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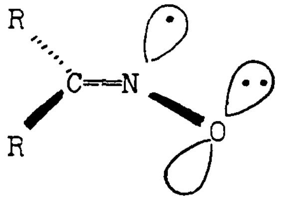
Many nitrogen containing molecules form stable neutral radicals, e.g., iminoxy radicals (3), the nitroxides (4), and heterocycles such as tetrazolinyl radicals (5).



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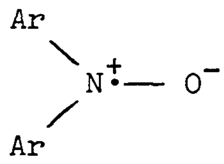

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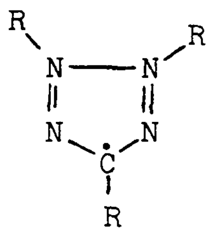


5

Addition of one electron to the LUMO of a diamagnetic π system gives a radical anion while removal of an electron from the HOMO forms the corresponding radical cation. Protonation and deprotonation can lead to neutral radicals.

$$R^{\bullet} \underset{+H^{+}}{\overset{-H^{+}}{\rightleftharpoons}} RH^{\bullet +} \underset{+e}{\overset{-e}{\rightleftharpoons}} RH \underset{-e}{\overset{+e}{\rightleftharpoons}} RH^{\bullet -} \underset{-H^{+}}{\overset{+H^{+}}{\rightleftharpoons}} RH_{2}{\bullet}$$

Electron transfer is not limited to one electron steps because of the disproportionation reaction shown below. The dissociation constant for the disproportionation is large in solvents of high dielectric constant, such as DMF or DMSO.

$$R \xrightarrow{2e} R^{=}$$

$$R + R^{=} \rightleftharpoons 2R^{\cdot -}$$

The spin label gives the molecule a paramagnetic handle, allowing examination in some detail of the MO containing the unpaired spin. One of the primary values of esr as a theoretical tool is the correlation of observed hyperfine splitting constants (hfsc) with spin densities calculated by MO methods. The magnitude of the hfscs, obtained by analyses of esr spectra, are related to the degree of interaction of the unpaired spin in the HOMO with nuclei of atoms in the radical with nonzero nuclear magnetic moment (*e.g.*, $M = \frac{1}{2}$: ^{1}H, ^{13}C, ^{15}N, ^{19}F; $M = 1$: ^{2}H, ^{14}N; $M = \frac{5}{2}$: ^{17}O). The amplitude of a spectral line arising from the hyperfine splitting of one particular atom will be proportional to the abundance of the interacting isotope in that (or equivalent) position in the molecule. Thus, the observation of hfscs from ^{1}H (100% natural abundance), ^{14}N (99.6%), and ^{19}F (100%) is more common than splitting from ^{2}H (1.5×10^{-2}%), ^{13}C (1.1%), ^{15}N (0.4%), or ^{17}O (0.04%) unless the molecules are isotopically enriched or the spectrum is of a high radical concentration with few, sharp lines.

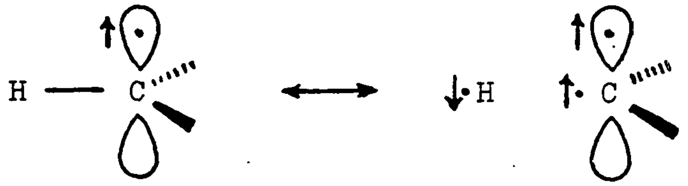
The simple Hückel calculation of an odd electron π system gives positive unpaired electron density values[1] resulting from a one electron function which represents the portion (or probability) of the electron at a particular trigonal atom. The sum of these probabilities equals one over the entire π system. The Hückel unpaired electron densities in many cases were found to be much smaller than those determined experimentally, particularly when the former values were very small or zero. An unpaired electron in the HOMO can interact with electron pairs populating lower lying orbitals, resulting in a partial unpairing, or polarization, of these spins affecting the magnitudes of spins on adjacent atoms (3,4). McLachlan has developed a perturbation treatment which can be applied to the simple Hückel calculation which in effect takes into account these polarizations (5). The net result is to impart spin of opposite sign on adjacent trigonal atoms so that atoms with zero or small unpaired electron density in the Hückel calculation become areas of negative spin density in the McLachlan calculation. The hfscs are absolute numbers in

---

[1] The usage of unpaired electron density and spin density is that suggested by J. R. Bolton (2).

a practical sense, since they do not distinguish between positive and negative values of spin density. The sum of the McLachlan spin densities over the π system is still unity.

Specifically, these interactions of atomic nuclei with unpaired spin may be of several types. First considered is that of an atom bonded to an sp² center containing spin density. Although the hydrogen lies in the nodal plane of the p orbital and might be expected to have zero interaction with the unpaired spin, the observed hyperfine splitting due to the hydrogen can be rationalized by a mechanism in which the carbon-hydrogen sigma bond is spin



polarized similar to the spin polarization of π-electrons previously considered. Again, spin polarization results in a negative spin on the adjacent (hydrogen) atom. McConnell has developed a simple quantative approximation for this interaction (6).

$$\underline{a}^H = Q^H_{CH}\ \rho^\pi_C$$

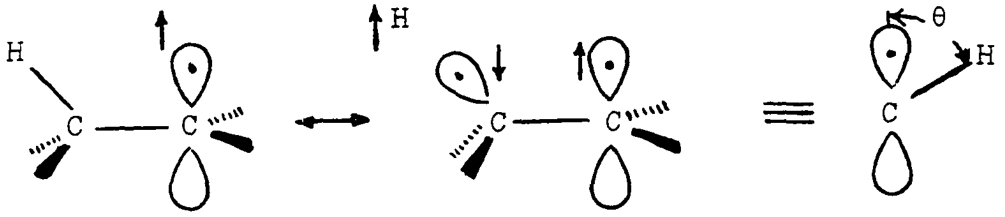
The spin density (ρ^{π}) and the hfsc ($\underline{a}$) are related by the factor Q_{CH}^{H}. The superscript refers to the nucleus responsible for the splitting and the subscript indicates the position of this nucleus relative to the center of spin density. Q is in gauss (1 gauss = 2.8×10^{6} MHz) and is negative. Q is in the range of -20 to -30 gauss and can change for different radicals due to a number of factors including charge type. More refined equations have been developed by Colpa and Bolton (7) and by Giacometti, Nordio, and Pavon (8).

The second type of I•S interaction is that of the nucleus of a trigonal atom with an electron in its p_z atomic orbital (or π molecular orbital) and is expressed by the Karplus-Fraenkel equation (9).

$$\underline{a}_i^M = (S_i^M + \sum_j \underline{Q}_{M_i X_j}{}^M)\,\rho_{M_j}{}^{\pi} + \sum_j \underline{Q}_{X_j M_i}{}^M\, \rho_{X_i}{}^{\pi}$$

The $\underline{a}^M$ is calculated taking into account contributions to the observed splitting constant from: 1) polarization of 1s electrons ($S_i{}^M$); 2) spin density on M, which is attached directly to X_j, through polarization of the 2s orbital of the M-X sigma bond ($\underline{Q}_{M_i X_j}{}^M$); and 3) spin density on neighboring atoms X_j, through the 2s orbital ($\underline{Q}_{X_j M_i}$), where ρ_{X_j} is the spin density at the neighboring atom. This approach has been used to calculate hfscs for nitrogen-14 (10,11), oxygen-17 (12), and carbon-13 (13).

A third type of spin interaction is a hyperconjugation delocalization applicable to sp^3 atoms alpha to the spin label.



The following relationship was put forth by Symons (14) as well as Heller and McConnell (15).

$$\underline{a}^{H}_{CCH_3} = (B_0 + B\cos^2\theta)\rho^{\pi}$$

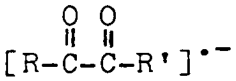
B_0, the residual interaction when $\theta = 90°$, is small and often ignored. B is a constant dependent on the charge of the radical, usually taken as 40 for anion radicals. The dihedral angle θ is defined in the drawing. If inversion or rotation of the group in question occurs on the ESR timescale ($\tau \approx 10^{-8}$ sec), a time averaged value of $\cos^2\theta$ must be used. Hyperconjugative delocalization falls off drastically with distance and only small hfscs, if any, are noticed for hydrogens beta to the sp^2 center in acyclic molecules.

Long-range spin interaction can occur if certain geometric requirements are met (W plan). These are usually observed in rigid, cyclic structures. No simple mathematical relationship exists for these long-range interactions. ESR provides a method for the study of these types of interactions which may possibly be manifested in other chemical properties of bridged systems such as reactivity and skeletal rearrangement during reaction.

The McLachlan modification of the simple Hückel calculations provides good correlation between hfscs and calculated spin densities in many radical systems. For bridged molecules and highly strained ring systems, more sophisticated calculation techniques are required.

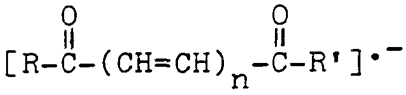
The Semidione Spin Label

One of the more extensively used spin labels is the semidione radical anion formed by addition of an electron to a conjugated diketone. Many aspects of the application of semidiones to chemical problems have been reviewed by Russell (16,17,18). The majority of this work has been done on 1,2-semidiones (6) derived from α-diketones. The possibility of vinylogous semidiones (7) exists and a



$[R-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-R']^{\cdot -}$

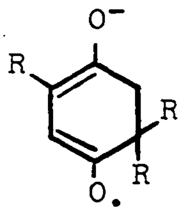
6

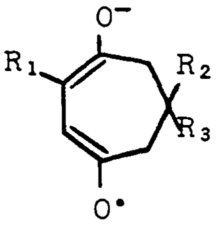


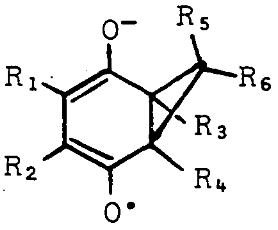
$[R-\overset{\overset{O}{\|}}{C}-(CH=CH)_n-\overset{\overset{O}{\|}}{C}-R']^{\cdot -}$

7

number of examples have been reported in cyclic structures. Examples of 1,4 semidiones are 8a (19), 8b (20), 9a,b (21), 9c,d (22), 10a,b,c (23), and 10d,e (24).





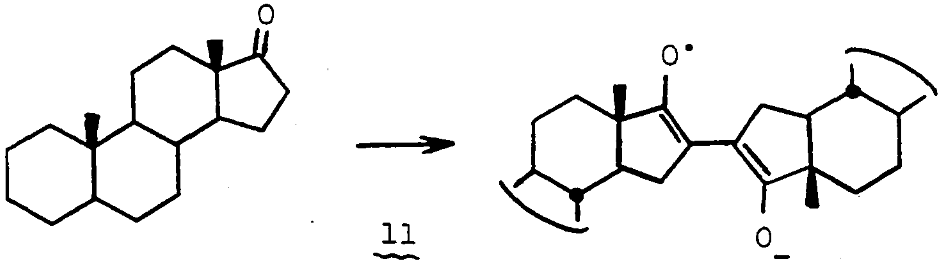


8a $R=H$
8b $R=CH_3$

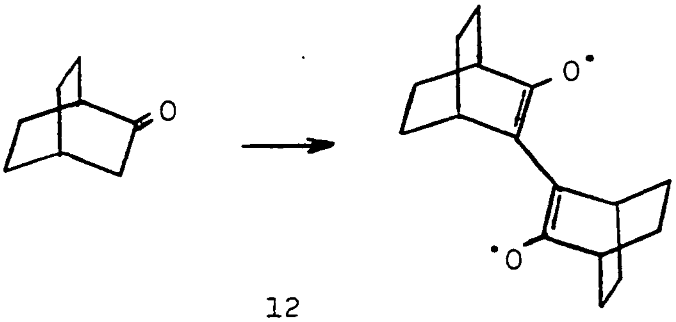
9a $R_1=R_2=R_3=H$
9b $R_1=R_2=R_3=CH_3$
9c $R_1=R_2=H$, $R_3=CH_3$
9d $R_1=H$, $R_2=R_3=CH_3$

10a $R_1-R_6=H$
10b $R_1-R_5=H$, $R_6=CH_3$
10c $R_1=R_2=R_3=R_4=R_6=H$, $R_5=CH_3$
10d $R_1-R_4=CH_3$, $R_5=R_6=H$
10e $R_1=R_3=R_4=H$, $R_2=R_5=R_6=CH_3$

1,4-Semidiones 11 (19) and 12 (25) result from condensations when the ketone precursor is treated with oxygen in the presence of base and DMSO.

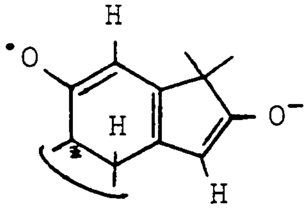


11



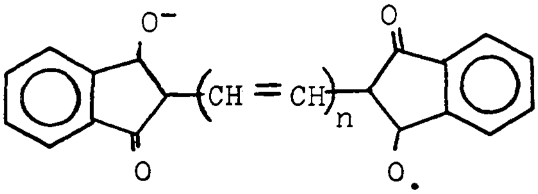
12

An example of a 1,6-semidione (13) results from treatment of 17,17-dimethyl-3a, hydroxy-18-nor-5β-androst-12-ene-11, 16-dione with potassium t-butoxide in DMSO (19).



13

A vinylogous series of 1,4-, 1,6-, and 1,8-semidiones has been prepared in the 1,1',3,3'-tetraketo-$\Delta^{2,2'}$-biindane system (14) (26).



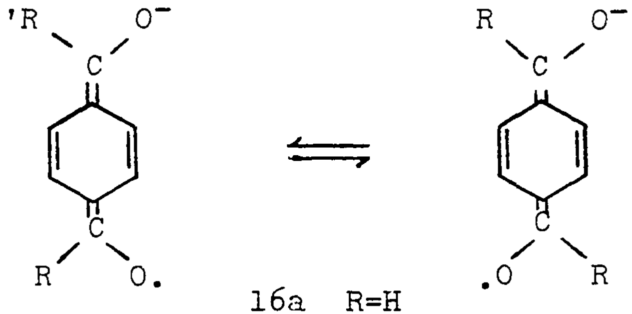
14 n = 0,1,2

Geometric isomers are possible with semidiones. It has been clearly demonstrated (27,28) that 1,2-semidiones can exist as separate cis-trans isomers (15a, 15b) in solution.

15a 15b

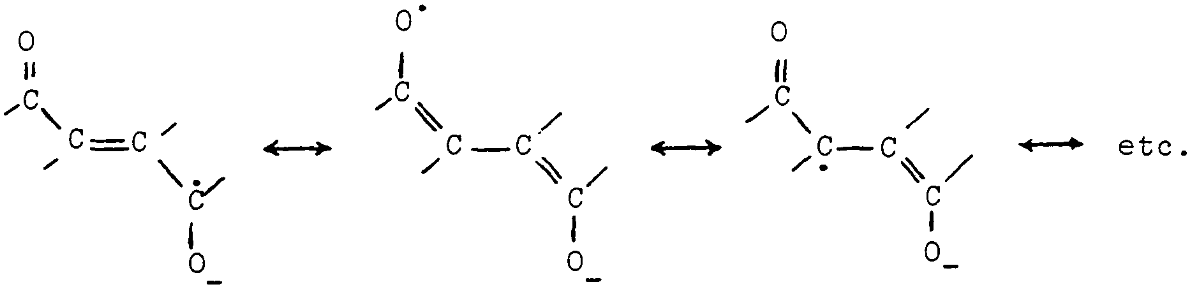
The trans structure is generally the more stable but if R and R' are not of great steric bulk the cis structure can be detected. In solvents of low dielectric constant and/or with the smaller gegenions such as lithium or sodium, which can coordinate to both oxygens, the cis can become the predominate isomer.

Phenylogs of semidiones have been reported and show cis-trans isomerism [16a (29, 30), 16b (31)].



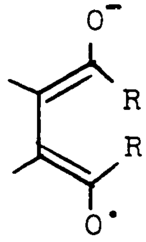
16a $R=H$
16b $R=CH_3$

The partial double bond character of π system of a 1,4-semidione due to resonance structures such as 17 leads to

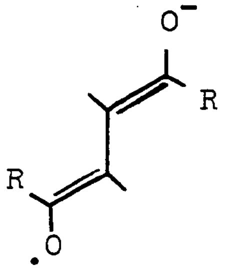


17

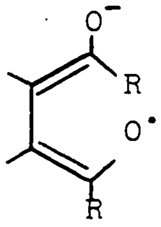
the possibility of six conformational isomers (18a-f).



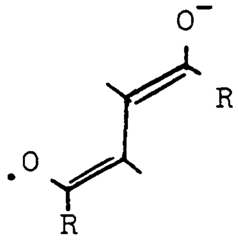
18a trans-cis-trans



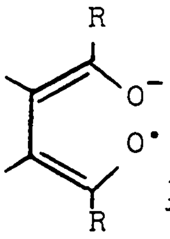
18d trans-trans-trans



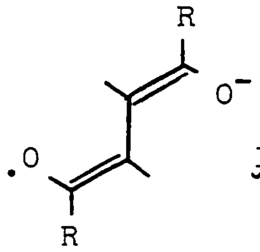
18b trans-cis-cis



18e trans-trans-cis



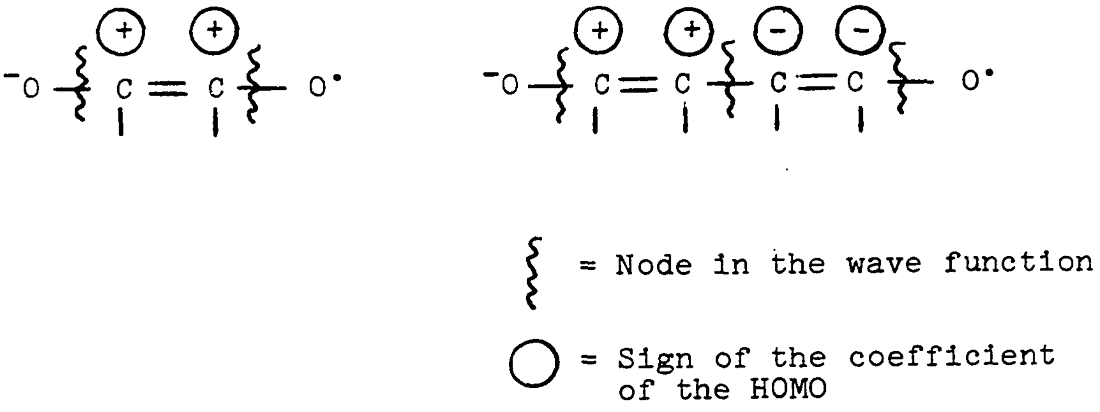
18c cis-cis-cis



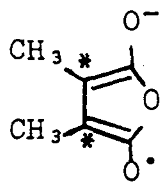
18f cis-trans-cis

The existence of six possible isomers was recognized by Nelsen (32) who reported cis-trans isomer mixtures for the anion radicals from diethyl maleate and diethyl fumarate.

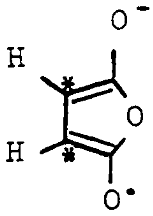
One of the interesting features of 1,4-semidiones is the change in symmetry of the HOMO going from the 1,2-spin label (ψ_3) to the 1,4-vinylog (ψ_4). The former has two nodes in the HOMO (containing the odd electron) while the latter has three, one bisecting the π system as shown below:



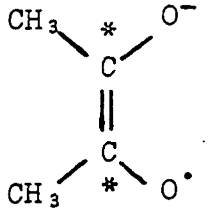
In addition, it is known that the radical anions 19 and 20 produced by the reduction of dimethyl maleic anhydride (33) and maleic anhydride (34) have spin densities on the starred



19 $a^H_{CH_3}$=6.10G



20 a^H_{CH}=6.79G



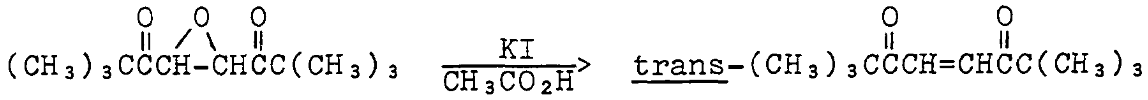
21 $a^H_{CH_3}$=6.9G

atoms in the same order of magnitude as those at the starred positions of dimethyl semidione (21) (35). The hfsc $a^H_{CH_3}$ is roughly the same as a^{H}_{CH} when a methyl group is substituted for hydrogen because $Q^{H}_{CCH_3} \cong -Q^{H}_{CH}$ ($\cos^2 \theta = 0.5$ for a freely rotating methyl group, therefore $B\cos^2 \theta = 40(0.5) \cong +24 = -Q^{H}_{CH}$). The similarity of spin density at the starred positions of **19** or **20** compared to **21** along with the sign differences of the HOMO coefficients at these positions gave impetus to prepare 1,4-semidiones to investigate the effect of symmetry of the HOMO of a spin label on long-range interactions of hydrogen atoms in the plane bisecting the spin label. Another goal of this work was to study the effect of cis/trans structure about the carbon-carbon double bond on spin distribution. As part of this effort the chemistry of the previously unknown acyclic 1,4-semidiones was investigated.

ACYCLIC 1,4-SEMIDIONES

Unsubstituted Double Bond

Reduction of the epoxide **22** with potassium iodide (36) gave the trans endione **23**. Photoisomerization of *trans*-**23**

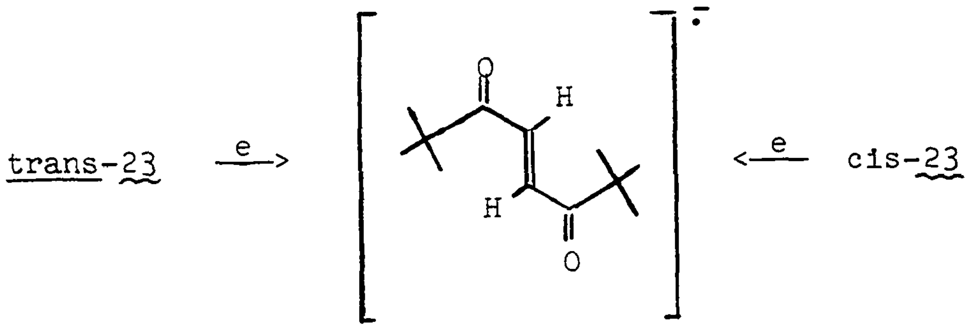


$$(CH_3)_3C\overset{O}{\overset{\parallel}{C}}\underset{\diagdown O \diagup}{CH-CH}\overset{O}{\overset{\parallel}{C}}C(CH_3)_3 \xrightarrow[CH_3CO_2H]{KI} \textit{trans}\text{-}(CH_3)_3C\overset{O}{\overset{\parallel}{C}}CH{=}CH\overset{O}{\overset{\parallel}{C}}C(CH_3)_3$$

22 **23**

at 2530Å gave *cis*-**23** (37). It was found that *trans*-**23** would quantatively convert to the cis isomer upon standing several weeks in sunlight.

When either *cis*- or *trans*-**23** was treated with potassium *t*-butoxide/DMSO or electrolyzed at the cathode in DMF, the same esr spectrum was obtained due to **24** (Figure 1). This



24 a^H = 5.50(2H), 0.20(18H)G

is presumably one of the isomers with a conformation *trans* about the central carbon atoms (**18d,e,f**).

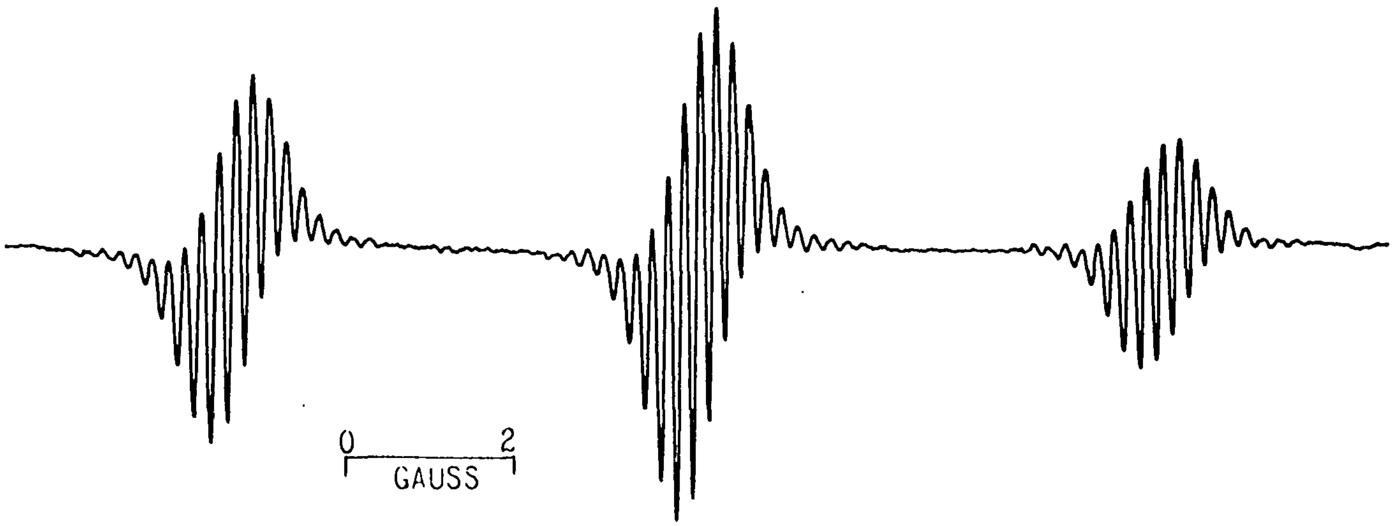
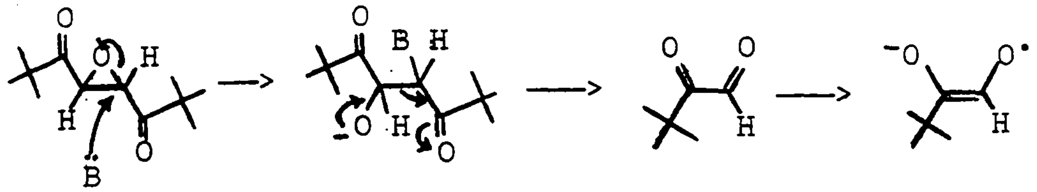


Figure 1. The first derivative esr spectrum of 2,2,7,7-tetramethyl-4-octene-1,4-semidione (**24**) in DMSO.

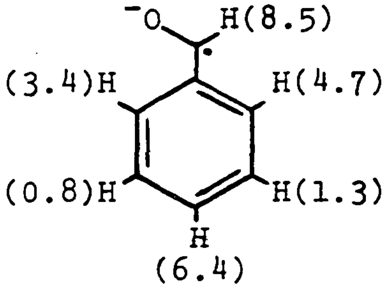
Treatment of the epoxide 22 with potassium *t*-butoxide/ DMSO or electrolysis in DMF gave a radical with a^{H}=8.6(1H) and 0.27(9H)G (Figure 2). This is similar to the spectrum from *cis*-*t*-butyl glyoxal radical anion (25) [Lit. a^{H}=8.7(1H) and 0.27(9H)G (27)].



22

25

trans-1,4-Diphenyl-2-butene-1,4-dione was reduced electrolytically in DMF to give a complex spectrum a^{H}= 4.71(2H), 1.10(2H), 0.59(2H), 0.50(2H), and 0.16(4H) (Figure 3). Assuming the two phenyl rings are equivalent, it follows that the ortho hydrogen atoms must be nonequivalent. A number of examples have been reported where nonequivalence of ortho hydrogens of a phenyl ring were observed. Most pertinent are the phenyl ketyls 26 (38) and 27 (39).



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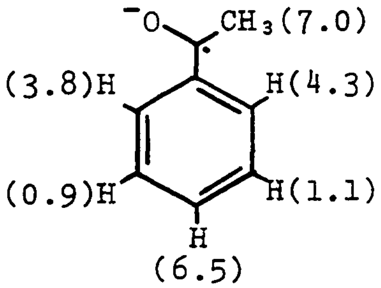

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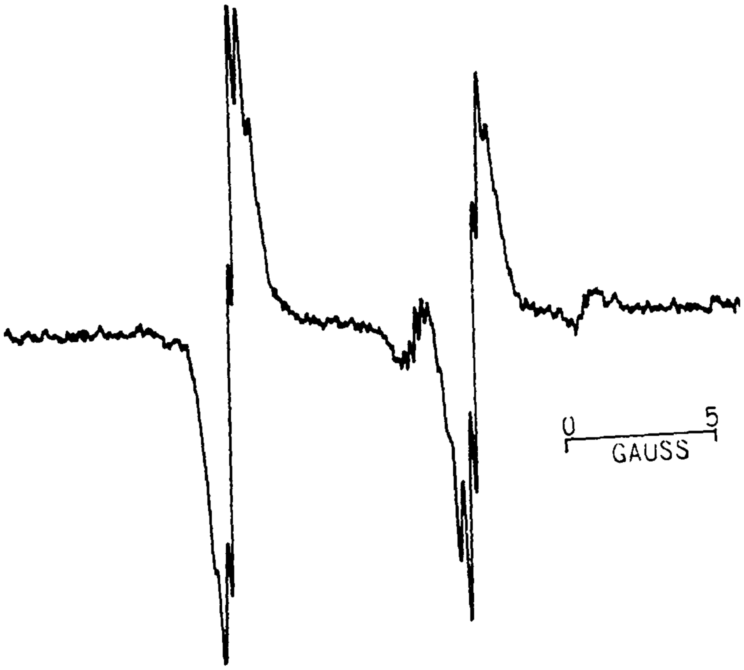
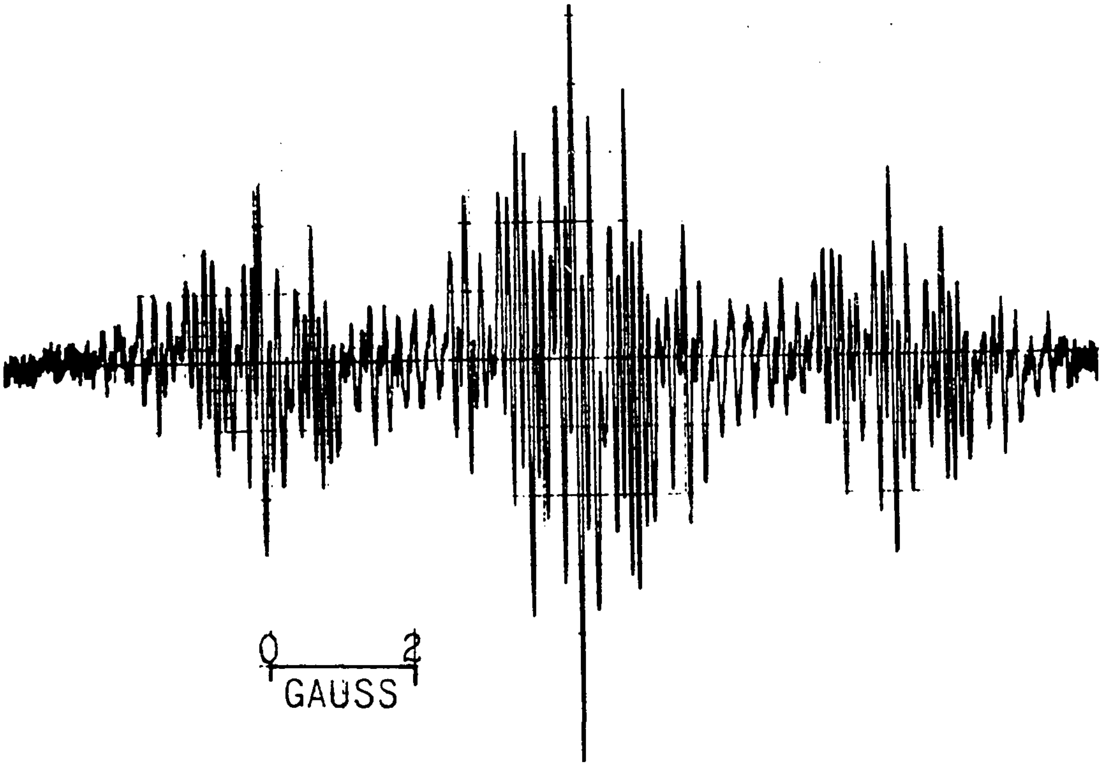


Figure 2. The first derivative esr spectrum of cis-t-butyl glyoxal radical anion (25) formed from 22 in DMSO.

Figure 3. The first derivative esr spectrum of *trans*-1,4-diphenyl-2-butene-1,4-semidione (**31**) (top) in DMSO; calculated spectrum (bottom) of middle multiplet for Lorentzian line width 0.06 gauss and splitting constants from text performed by JEOLCO JNM-RA-1 spectrum accumulator.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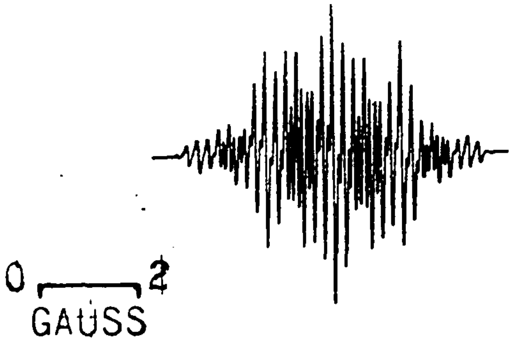
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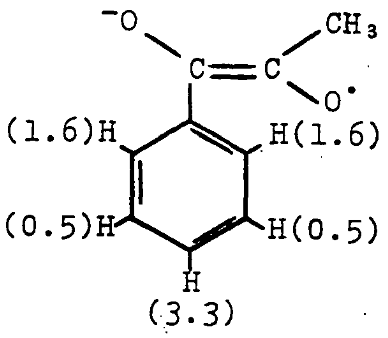
Phenyl-1,2-semidiones 28 and 29 (31) have equivalent ortho



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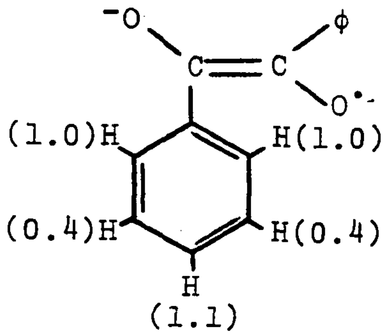
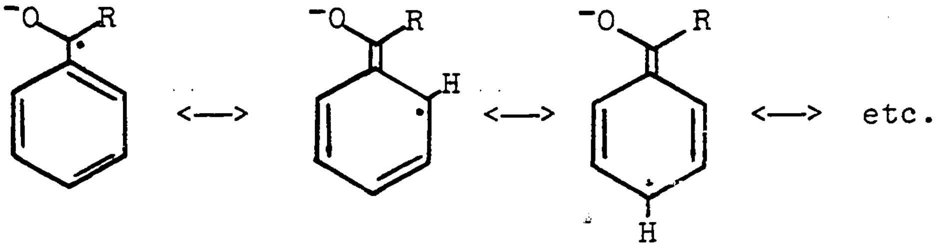


29

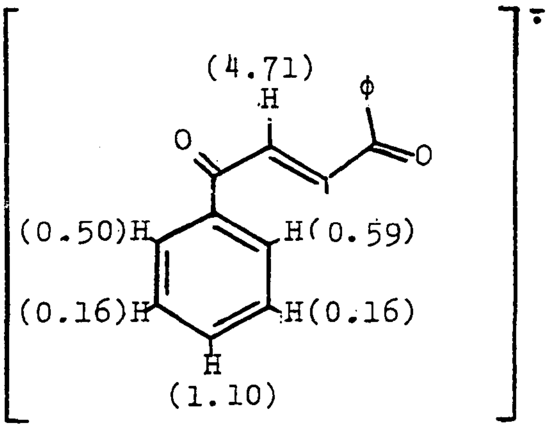
hfscs. The nonequivalence of the ketyl hydrogens was interpreted as due to a high bond order of the carbonyl carbon-phenyl bond in 26 and 27. This results from extensive delocalization into the ring as in 30 and is reflected in large hfscs of the ring hydrogens. The high



30

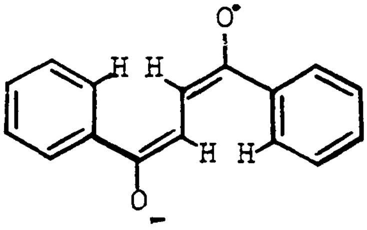
bond order raises the energy requirement for rotation in the ketyls while semidiones 28 and 29 with smaller hfscs in the ring are freely rotating on the esr timescale.

The hfscs of diphenyl-1,4-semidione were assigned as shown in 31. The spin density in the rings of 31 is about

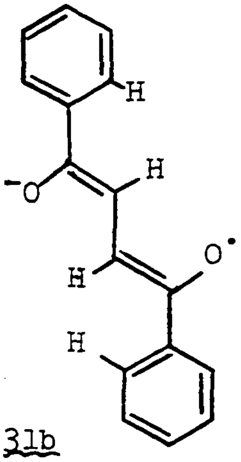


31

the same as that of diphenyl semidione 29 indicating the phenyl group should be freely rotating from electronic consideration. A steric interaction that interferes with free rotation is possible if the semidione 31 assumes a trans-trans-trans conformation (31a).



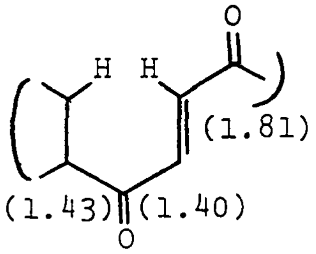
31a trans-trans-trans



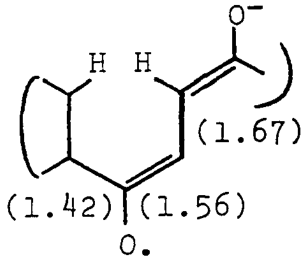
31b

cis-trans-cis

Molecular models (Dreiding) of the parent dione indicate the hydrogen-hydrogen bond distance shown in 31a is of the order of several tenths of an angstrom. A minor shortening of this distance would take place going from the diketone to the radical anion as indicated by the calculated bond orders for the diketone (32a) and radical anion (32b) shown below.

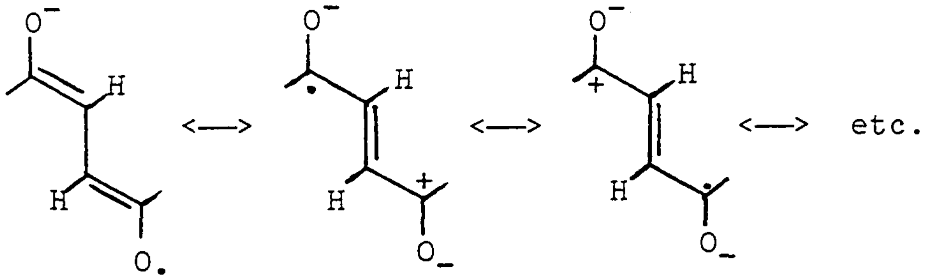


32a



32b

If the cis-trans-cis geometry (31b) is assumed, the hydrogen-hydrogen distance shown is considerably greater than 31a and the phenyls should be freely rotating in this conformation. A possible explanation for the preference of 31a over 31b is that of the effect of electrostatic repulsion of the partially negatively charged oxygen atoms on the energy of the radical ion (33). Molecular models

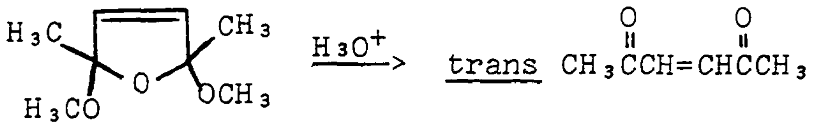


33

(again of the parent diketone) show the oxygens in **31a** are 1.0-1.2Å farther apart than in **31b** and may result in stabilization of **31a**.

Another geometric possibility is the *trans*-*trans*-*cis* (**18e**). In this case it could be postulated the hfsc assignment should be that of two sets of equivalent ortho hydrogen splittings in two nonequivalent rings. The identical splittings of the para and vinyl hydrogens mitigates against this argument. Any interconversion of isomers by rotation of the carbonyl carbon-vinyl carbon bond would tend to allow free rotation of the phenyl groups and average the splittings from the ortho hydrogens. The possibility of isomer **18a**,**b**, or **c**, (cis about the central bond) can be discounted *vide infra*.

trans-3-Hexene-1,4-dione (**34**) was prepared by hydrolysis of the cyclic diketal **35**, itself the product of bromination of 2,5-dimethylfuran in methanol (40). As with **23** the material photoisomerized to the *cis* upon standing several weeks in sunlight. Electrolysis of either *cis*-**34** or *trans*-**34** in DMF or *cis*-**34** at -80° in THF gave only weak unresolved

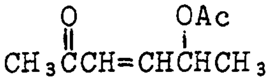


$$\xrightarrow{H_3O^+} \textit{trans}\ CH_3\overset{O}{\overset{\|}{C}}CH{=}CH\overset{O}{\overset{\|}{C}}CH_3$$

35 **34**

signals. A flow experiment with *trans*-(34) and potassium *t*-butoxide in DMSO gave a strong, resolvable signal resulting from two or more radicals with different G values (Figure 4). The total spectrum width was 37G. A triplet of septets could not be seen in the spectrum.

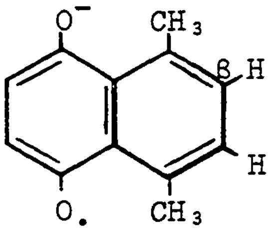
Treatment of *cis*-34 with potassium *t*-butoxide in DMSO under static conditions gave no signal. A mixture of *cis*-34 and 36 when treated under the same conditions gave a



$CH_3\overset{\overset{O}{\|}}{C}CH{=}CH\overset{\overset{OAc}{|}}{C}HCH_3$

36

strong signal (Figure 5) with a^H=3.0(2H), 2.2(2H), 0.6(6H)G. The number of hydrogens interacting indicates a radical of high symmetry, possibly a product resulting from condensation. The magnitudes of the hfscs indicate the possibility of semiquinone formation. While the β hydrogens of the napthaquinone 37 should have a smaller hfsc (0.6G) than those observed (2.2G), either the dihydro (38) or tetrahydro (39) derivatives can be considered. Treatment



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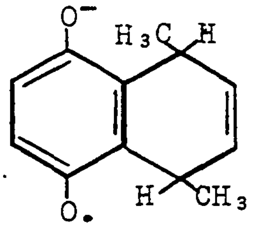
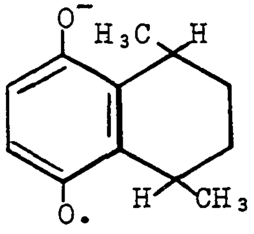


38



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of 36 with potassium *t*-butoxide/DMSO gave no signal.

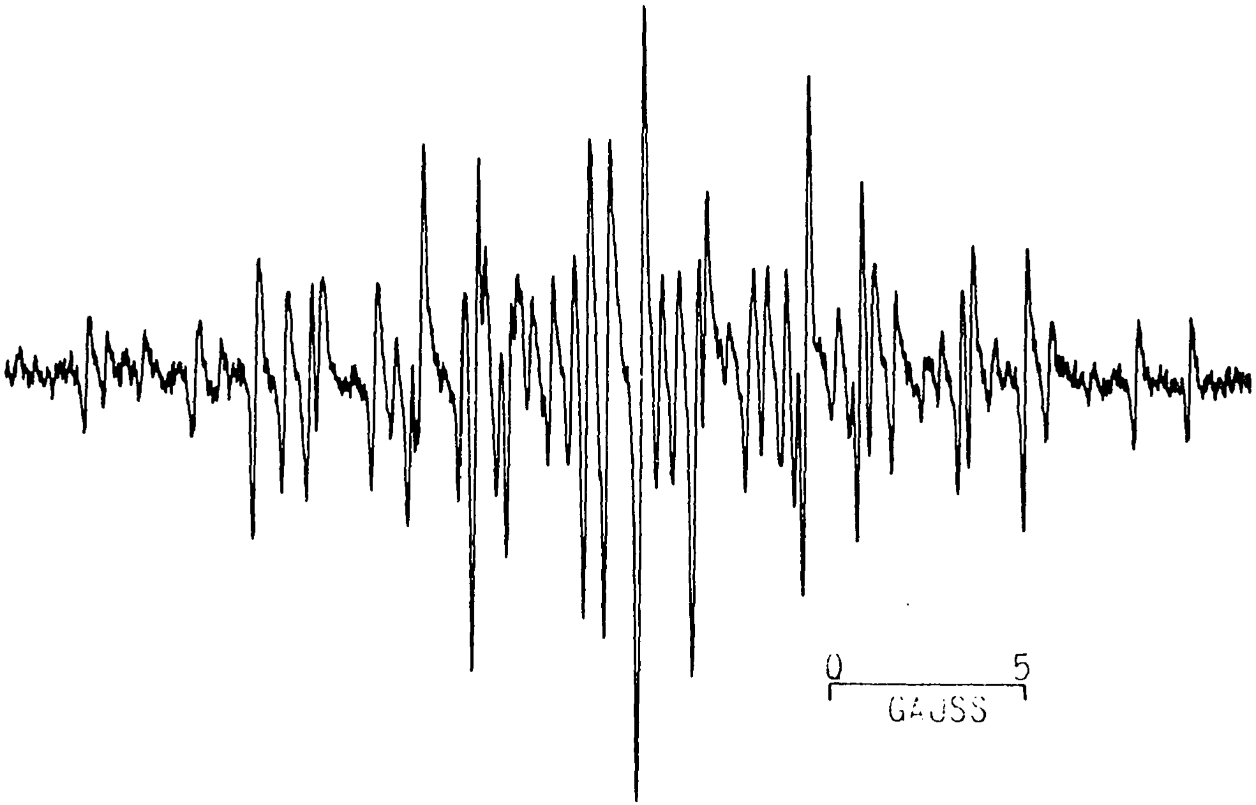
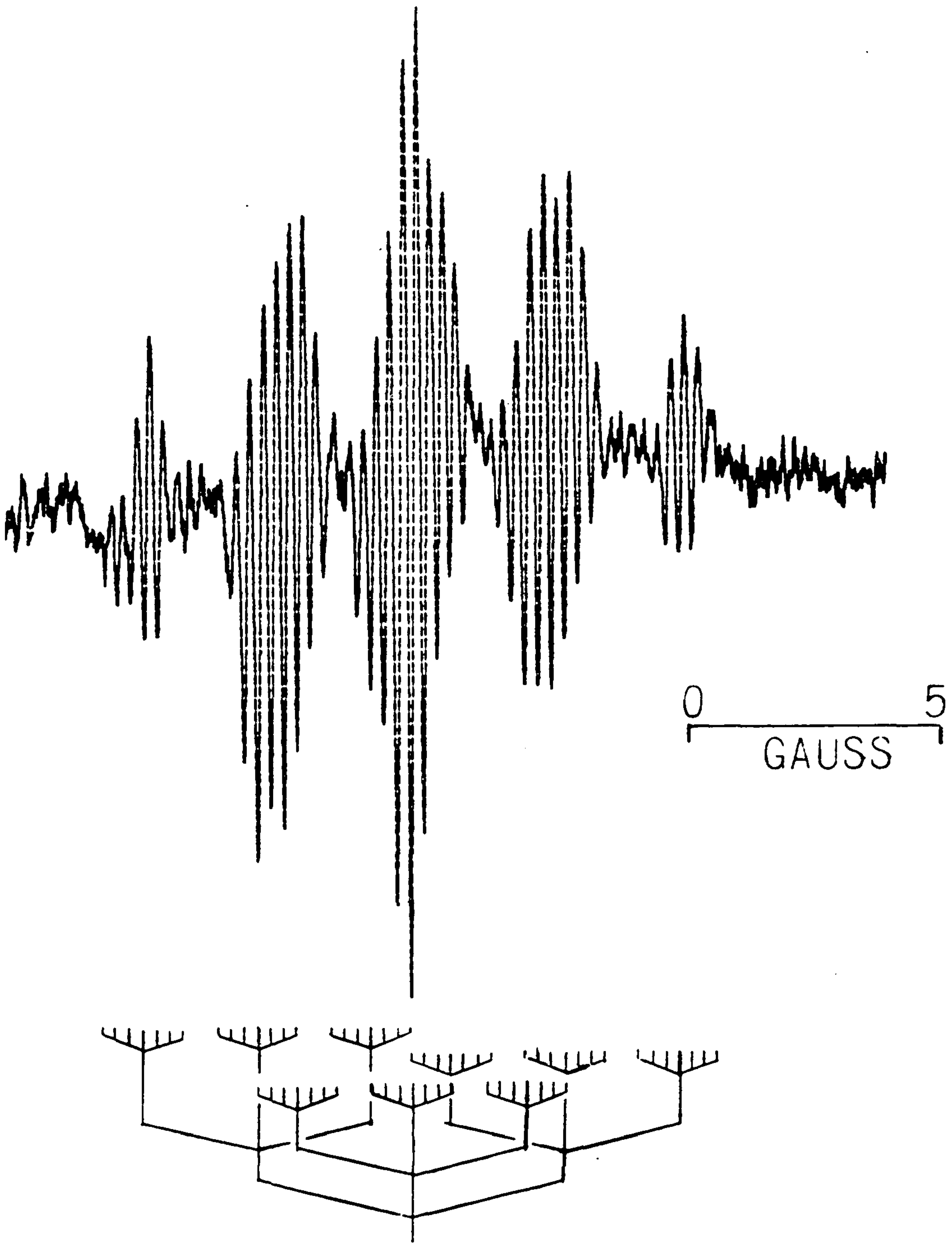


Figure 4. The first derivative esr spectrum of the radicals from *trans*-3-hexene-2,5-dione (**34**) in DMSO.

Figure 5. The first derivative esr spectrum of the radical obtained from a mixture of *cis*-3-hexene-2,5-dione (34) and 5-acetoxy-3-hexen-2-one (36) in DMSO.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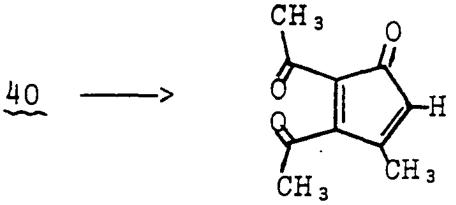
Tetraacetylethylene (40) was prepared by the method of Adembri *et al*. (41). When reduced electrolytically at ambient temperature in DMF or at -80° in THF, no signal was seen. This is somewhat surprising in view of the low half-wave reduction potential of 40 (Table 1). When treated with lithium in hexamethylphosphoric triamide (HMPA) a spectrum was recorded and tentatively analyzed as $\underline{a}^{H}=2.04(3H)$, 1.76(1H), 0.65(3H), and 0.31(3H)G, (Figure 6). A condensation-dehydration of one half of the molecule could lead to 41. The calculated hfscs for a radical ion

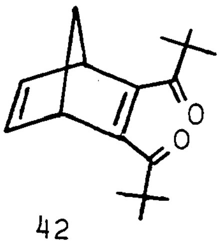


41

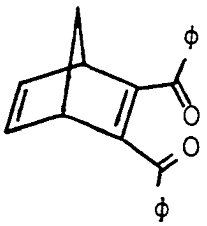
corresponding to this structure are $\underline{a}_{A}^{H}=0.38$, $\underline{a}_{B}^{H}=0.60$, $\underline{a}_{C}^{H}=2.65$, and $\underline{a}_{D}^{H}=2.52$G (see Appendix).

cis Substitution at the Double Bond

Structure 42 is the Diels Alder adduct of cyclopentadiene and dipivaloylacetylene. The diphenyl analog 43 was



42



43

Figure 6. The first derivative esr spectrum of the radical from tetraacetylethylene (40) in HMPA.

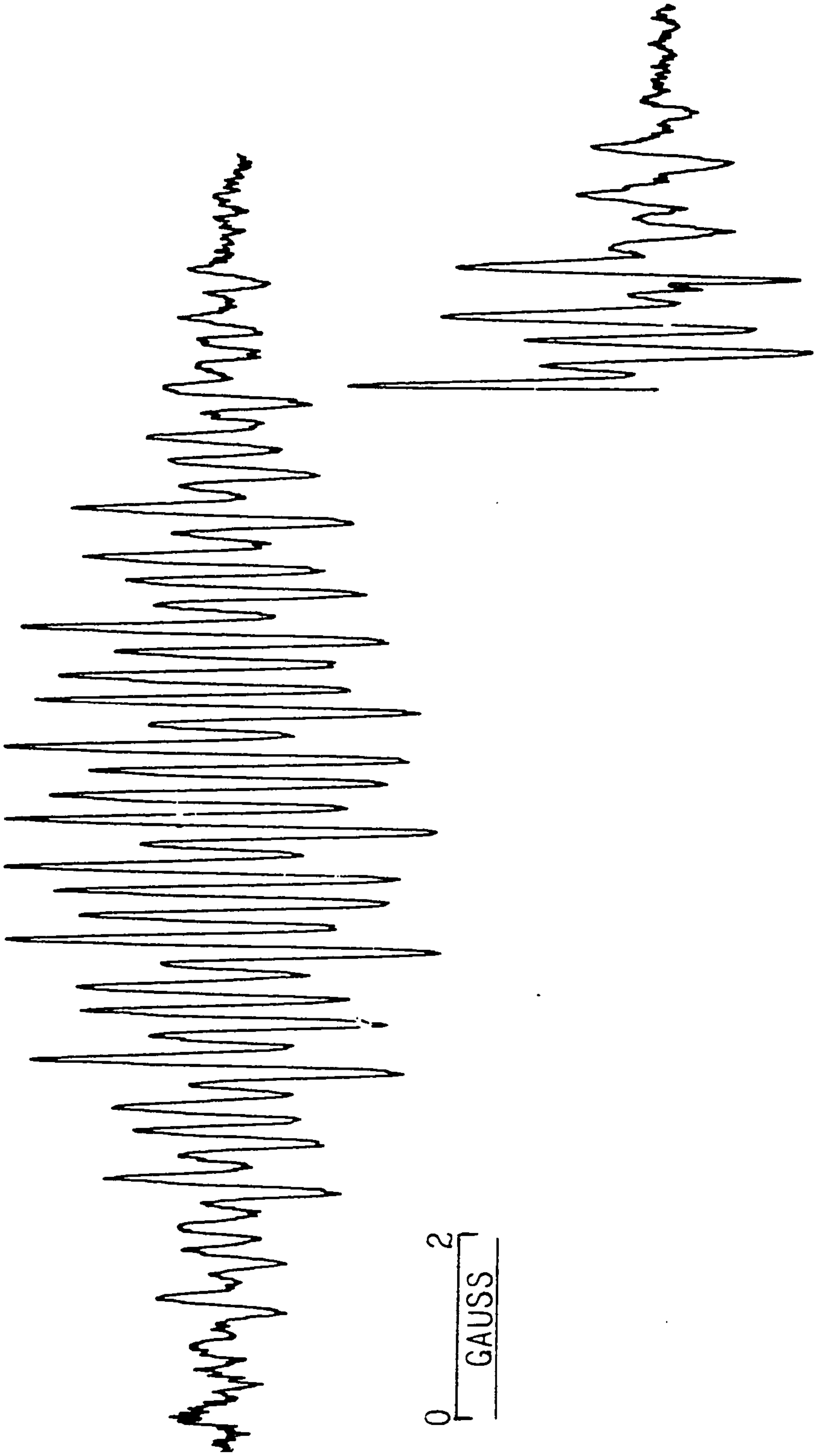

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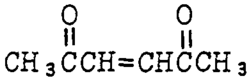
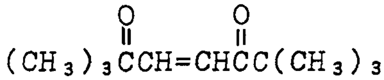
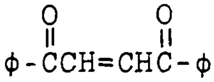
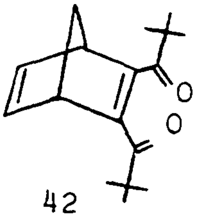
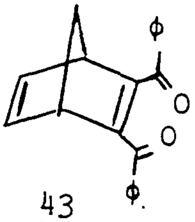
Table 1. Half-wave reduction potentials of unsaturated diketones[a]

	$E_{1/2}$ (vs. SCE)
cis  $CH_3\overset{\overset{O}{\|}}{C}CH{=}CH\overset{\overset{O}{\|}}{C}CH_3$ 34	-1.10[b], -1.40[b]
cis  $(CH_3)_3\overset{\overset{O}{\|}}{C}CH{=}CH\overset{\overset{O}{\|}}{C}C(CH_3)_3$ 23	-1.14
 $\phi\text{-}\overset{\overset{O}{\|}}{C}CH{=}CH\overset{\overset{O}{\|}}{C}\text{-}\phi$ 32a	-0.95
$Ac_2C{=}CAc_2$ 40	-0.17[b]
 42	-1.64[b]
 43	-1.33[b]

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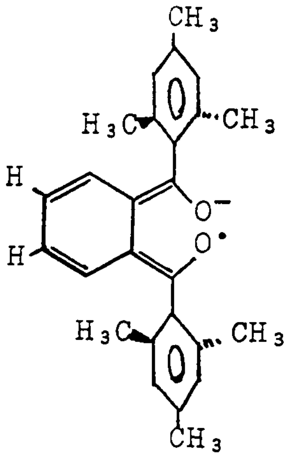
[a] Dropping mercury cathode; 0.001 N DMF solution; 0.1 N in n-$Bu_4N^+ClO_4^-$ depolarizer.

[b] Irreversible wave.

also studied. Steric requirements constrain the endione portion of these adducts to a cis-cis-cis (18a) conformation. The proximity of the oxygens is a destabilizing factor in the corresponding radical anion due to electrostatic repulsion. The half-wave potentials of 42 and 43 (Table 1) reflect this.

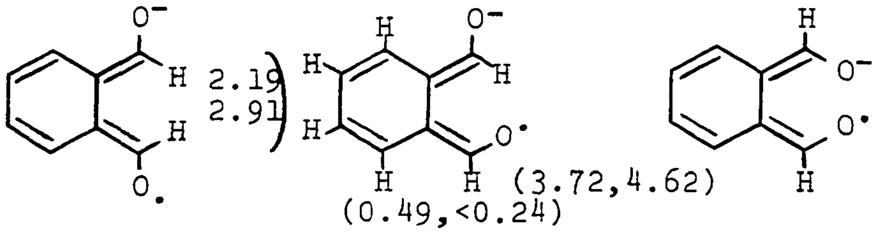
A similar steric situation arises in the investigation of the alkali metal reduction of o-dimesitoylbenzene in DME to give the radical anion 44 (42). The only splitting observed was from the β hydrogens shown (2.52-2.65G depending on the cation) and from the cation itself. The mesitylene rings were at right angles to the dione π system containing the unpaired spin because of steric interaction.



44

A situation where any of the three cis geometries 45a,b, or c is feasible on steric grounds was studied by Stone and

Maki (30). The phthaldehyde anion radical 45 was found to have five splitting constants, each arising from one hydrogen.

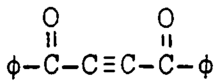


45a 45b 45c

The cis,cis,trans conformation 45b was necessary to account for hydrogen nonequivalence and it was estimated that 45b was the most stable conformation by at least 1.7 kcal/mole.

Potassium metal reduction of 42 in THF at -80° gave a signal that died too quickly to be recorded. Electrolysis of 42 in DMF at -30° gave a poorly resolved spectrum consisting of a^H=4.8(1H) and 0.3(>12H)G. Reduction with potassium in HMPA gave an envelope with a^H=0.38(>18H)G which decayed to a complex spectrum upon standing.

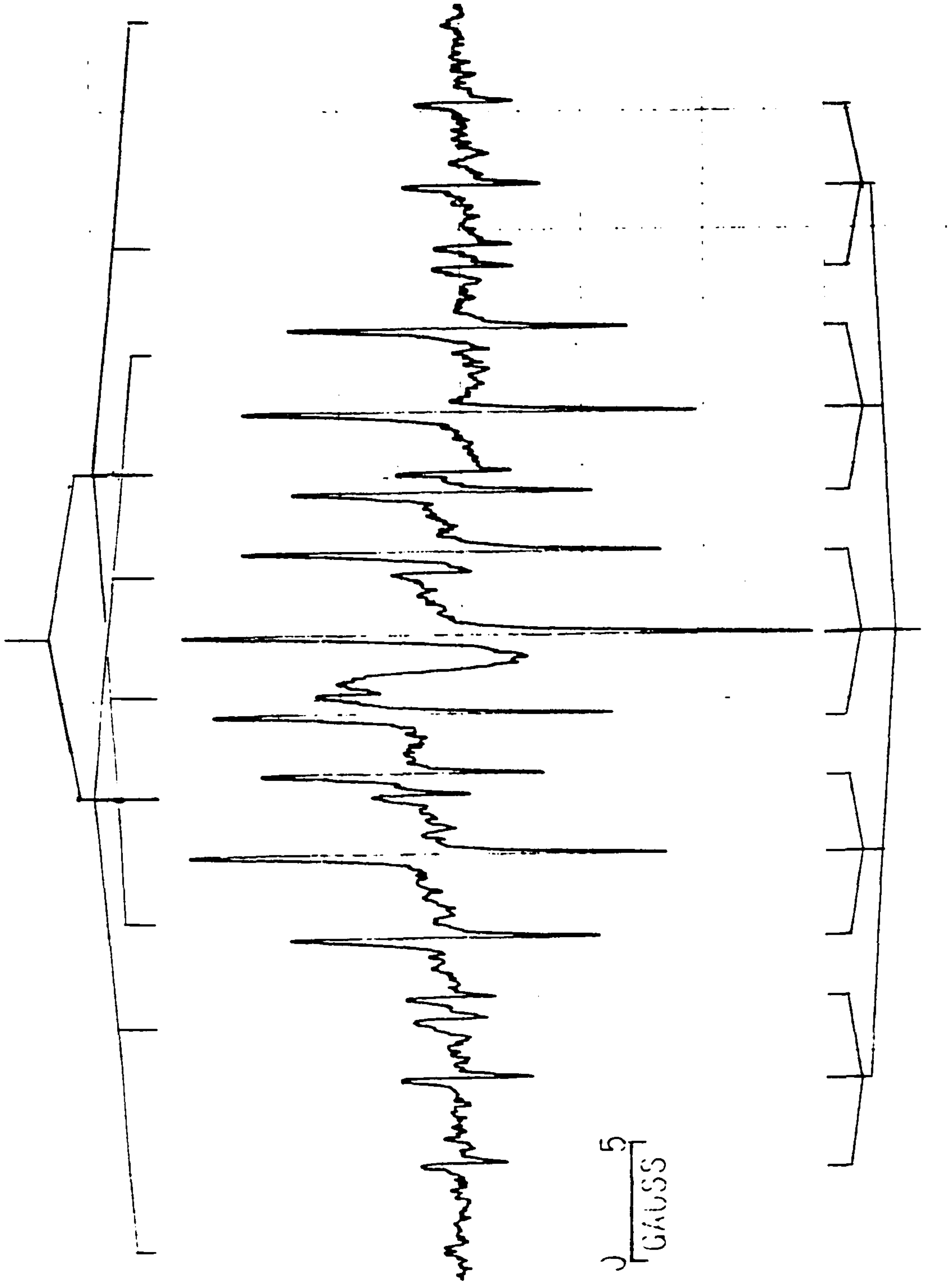
Treatment of 43 with potassium t-butoxide/DMSO under flow conditions gave no signal. However, lithium/HMPA reduction gave two radicals: major, a^H=9.5(4H) and 3.6(2H)G; minor, a^H=13.6(1H) and 9.4(4H)G (Figure 7). The dione (46) resulting from the reverse Diels Alder reaction of 43



$$\phi-\overset{O}{\overset{\|}{C}}-C\equiv C-\overset{O}{\overset{\|}{C}}-\phi$$

46

Figure 7. The first derivative esr spectrum of the radical from 2,3-dibenzoylbicyclo[2.2.1]-2,5-heptadiene (43) in HMPA.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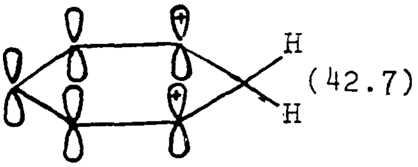
was treated with lithium/HMPA. A complex signal resulted. However, neither radical resulting from **43** appeared to be present. The results obtained with **42** and **43** seem difficult to rationalize in terms of the known chemistry of these systems.

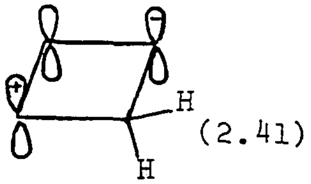
THE 1,4-SPIN LABEL CONTAINED IN A RING

Monocyclic 1,4-Semidiones

A brief discussion of the consequences of HOMO symmetry on spin transmission is pertinent. Whiffin (43) first related the hfsc of a methylene interacting with two equivalent spin sites to the square of the sum of the coefficients $(c_1+c_2)^2$ of adjacent atoms for the HOMO containing the odd electron. This allowed him to account for

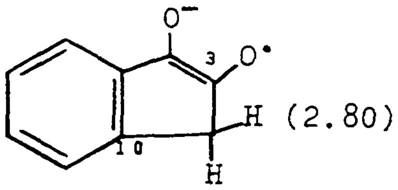


47 ψ_3



48 ψ_2

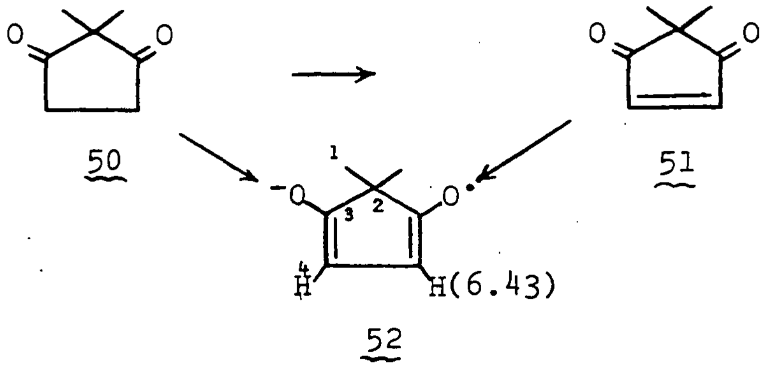
the methylene splitting of cyclohexadienyl radical 47 which was much larger than that predicted by relationships summing spin densities *i.e.* $(c_1^2+c_2^2)$. Whiffin also postulated that the cyclobutenyl radical 48 would have zero methylene splitting. Very small methylene splittings were subsequently found for 48 by Krusic *et al.* (44). The methylene splitting of 49 was found to be much smaller than predicted by a



49

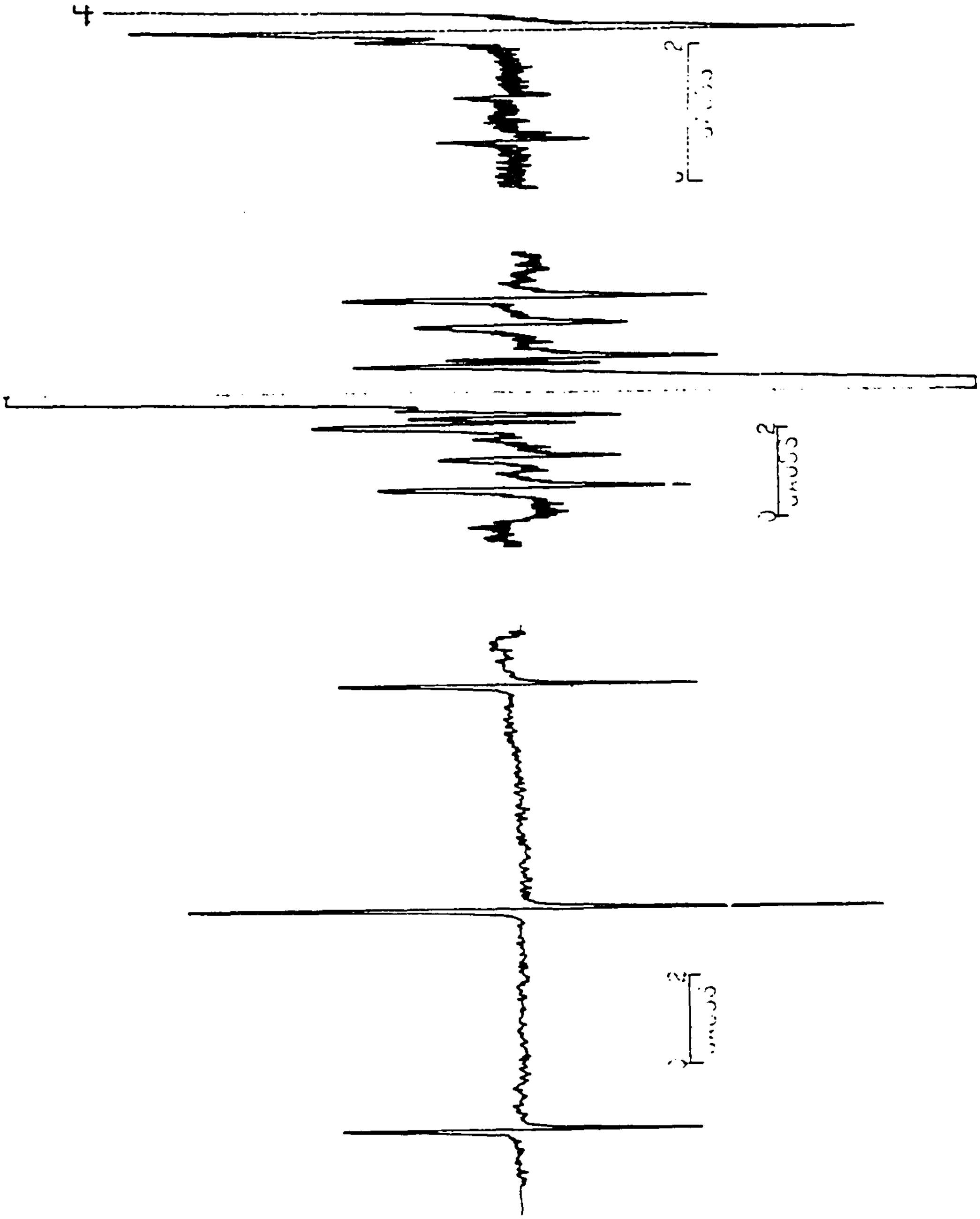
$(\rho_3+\rho_{10})$ function (45,46). The coefficients of ψ_6 are of opposite sign at positions 3 and 10. This demonstrated that partial cancellation of methylene hfsc by adjacent spin sites with coefficients of opposite sign in the HOMO is not limited to the nodal plane of a symmetric system.

2,2-Dimethylcyclopentane-1,3-dione (50), when brominated with NBS, eliminates hydrogen bromide spontaneously under reaction conditions to give 51. Reduction of 51 either electrolytically in DMF or by treatment with potassium *t*-butoxide/DMSO gave semidione 52 (Figure 8a). Only two



hydrogens are seen, the *gem*-dimethyl being in the nodal plane of ψ_4. A spectrum identical to Figure 8a is obtained by treatment of 50 with potassium *t*-butoxide and oxygen/ DMSO. A well resolved ^{13}C spectrum (natural abundance) is observed (Figure 8b) with a^C=4.30(2C), 3.00(1C), 1.40(2C), and 1.14(2C)G. From elementary MO considerations (see Appendix) we know $a_4^C > a_3^C$, but it is not obvious which of the three sets of hfscs belong to positions 3 and 4 of 52. The

Figure 8. The first derivative esr spectrum (left) of 2,2-dimethylcyclopent-4-ene-1,3-dione radical anion (52) in DMSO; ^{13}C spectrum of enlarged central peak (middle); and ^{13}C spectrum of side of central peak for 12% ^{13}C methyl enriched 52 in DMSO (right)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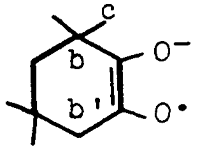
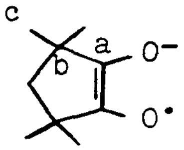
2
2

mechanisms of ^{13}C hyperfine interaction results in considerable variation between a^c and a^H of the attached hydrogen atom, e.g. 53 and 54 (27). Compound 50 was prepared with



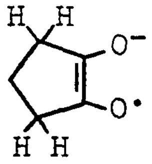
$a^H_{b'}=8.9(2H)G$
$a^c_{b',b,c}=4.4(4C)G$

53



$a^c_{b,c}=5.9\pm.1(6C)G$

54a

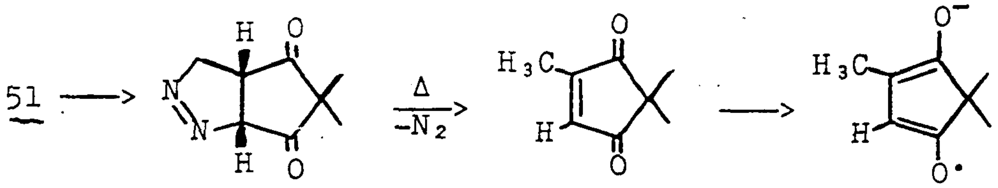


$a^H=13.4(4H)G$

54b

^{13}C enrichment at the methyl group (12% ^{13}C total incorporation from P+1 corrected for natural abundance at other positions). The esr spectrum (Figure 8c) for this material shows that the 1.14G splitting was due to the gem dimethyl carbons.

The methyl analog (56) of 51 was prepared by treatment of 51 with diazomethane and pyrolyzing the resulting pyrazoline 55 in refluxing toluene. Treatment of 56 with potassium t-butoxide/DMSO gave 57, $a^H=6.50(3H)$ and $5.81(1H)G$ (Figure 9).



55 56 57

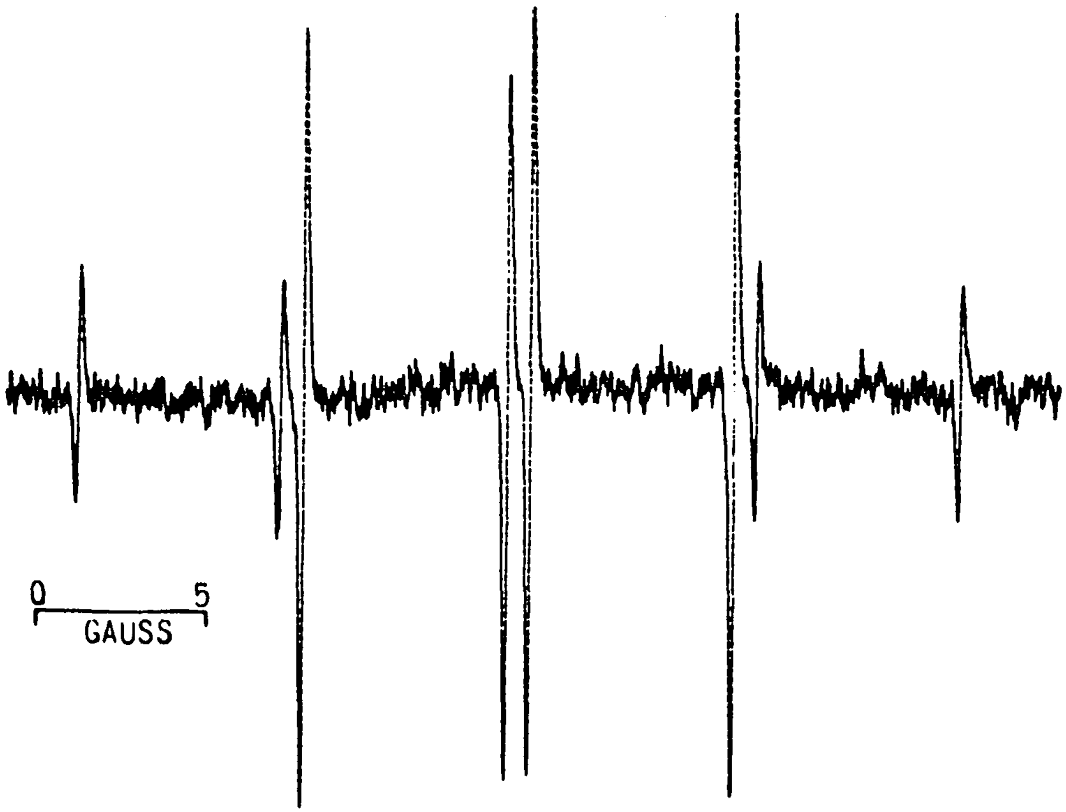
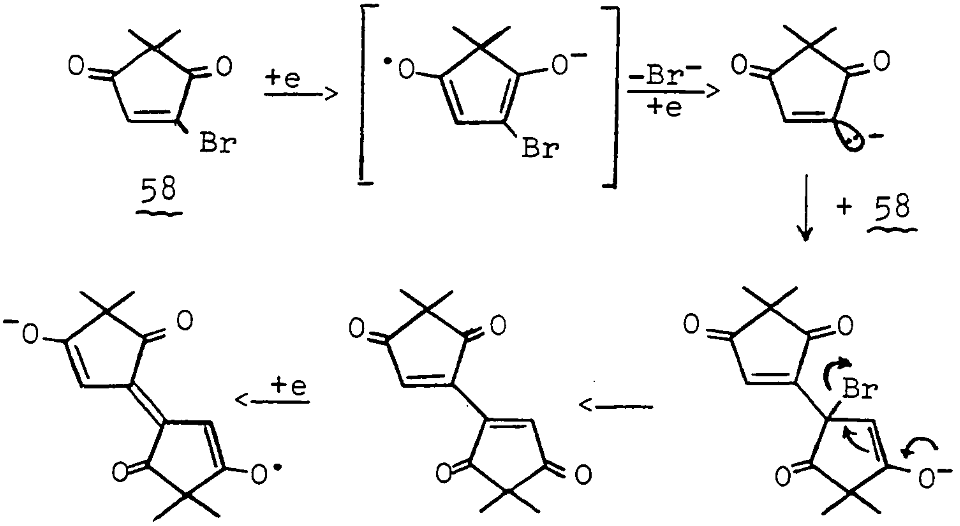


Figure 9. The first derivative esr spectrum of 2,2,4-trimethylcyclopent-4-ene-1,3-dione radical anion (57) in DMSO.

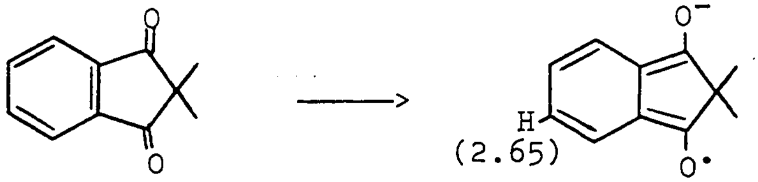
Bromination of 51 with one mole of bromine accompanied by loss of hydrogen bromide gave the monobromide 58. Electrolysis of 58 gave a signal believed to result from the radical ion of dimer (59), $\underline{a}^H$=4.2(2H)G (Figure 10).



58

59

The indanedione 60 was prepared by the method of Wislicenus and Kotzle (47). Electrolytic reduction gave 61,



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61

the benzo analog of 52. This signal appears as a broad triplet in DMF (Figure 11) with $\underline{a}^H$=2.65(2H)G. Nelsen (48)

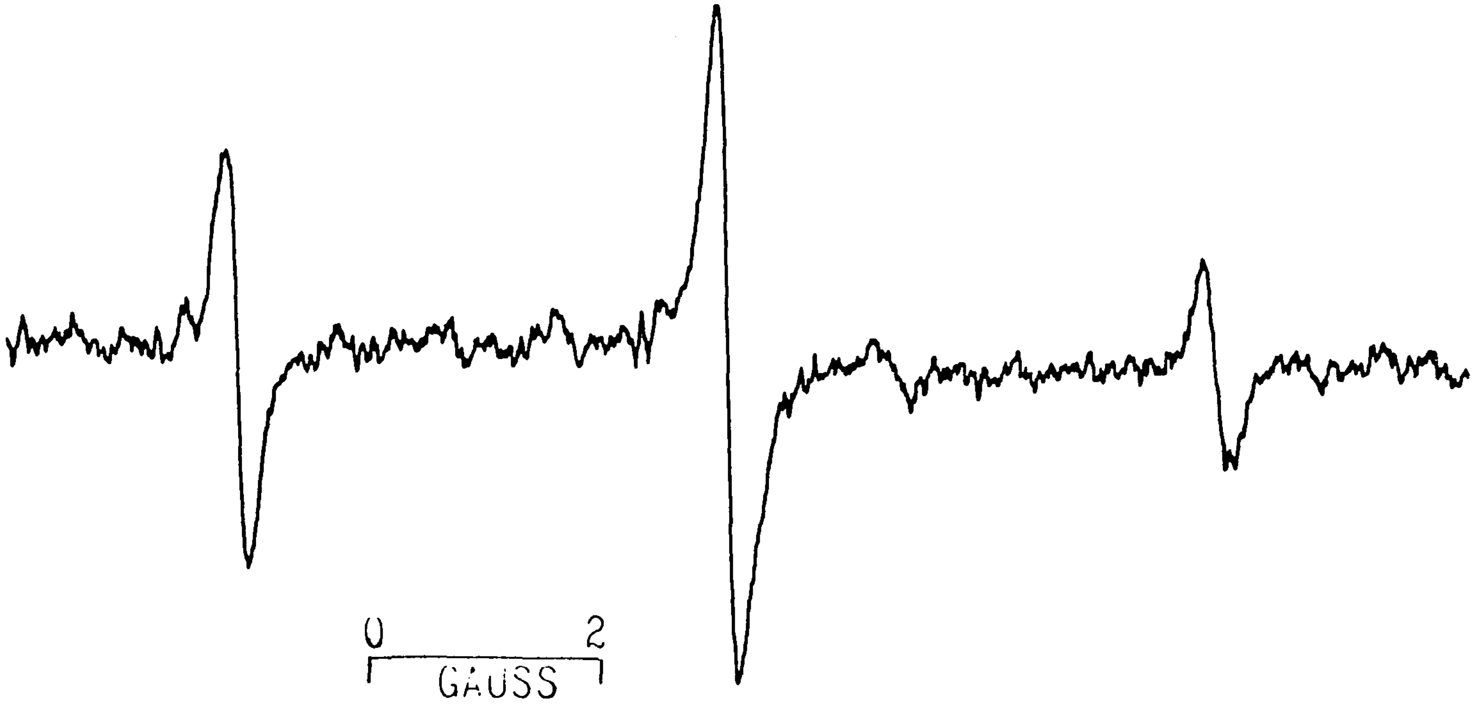


Figure 10. The first derivative esr spectrum from electrolytic reduction of 4-bromo-2,2-dimethyl-4-cyclopentene-1,3-dione (58) in DMF.

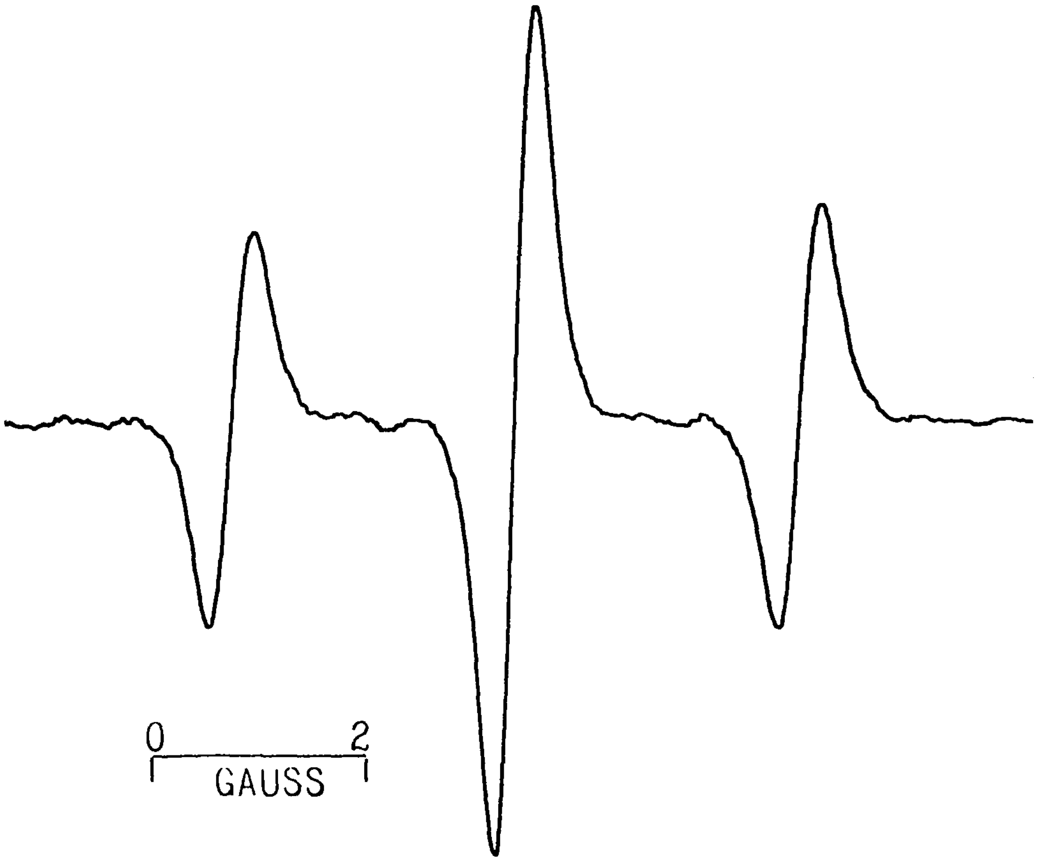
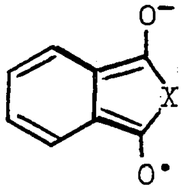


Figure 11. The first derivative esr spectrum of 2,2-dimethyl-1,3-indanedione radical anion (61) in DMF.

has produced the anion and dianion radicals 62. Better

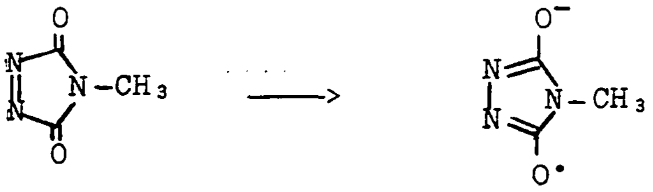


X = O,S,NH,NCH_3,CH^-,CCH_3^-

62

resolution was obtained in some instances by lowering the temperature to -40° (49). When 60 was electrolyzed in DMF at -30° or in THF at -60°, no further resolution of the large triplet resulted. The radical ion resulting from reduction of 2-methyl-2-phenyl-1,3-indanedione has been reported (50).

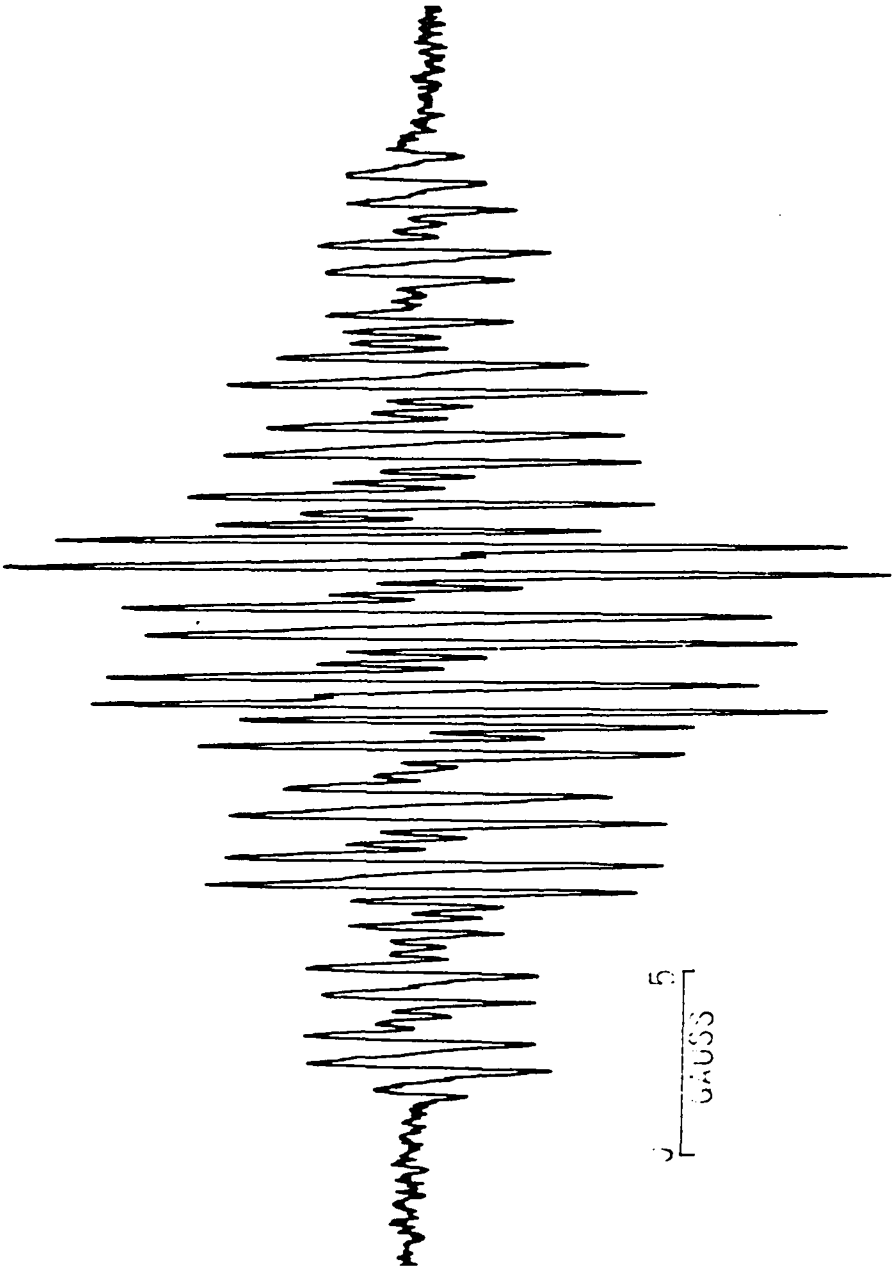
The triazolinedione 63 (51,52), a heterocyclic analog of 51, was electrolytically reduced in DMF to give 64,



63 64

$\underline{a}^N$=4.87(2N) and 1.85(1N), $\underline{a}^H$=0.75(3H) (Figure 12). The low spin density in the nodal plane is reflected in the small hfscs of the $N-CH_3$.

Figure 12. The first derivative esr spectrum of 4-methyl-1,2,4-triazoline-3,5-dione radical anion (64) in DMF.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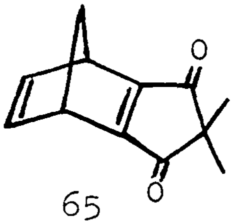
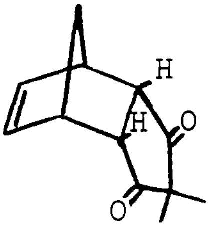
Cyclic 1,4-Spin Labels in Bridged Structures

The dione 65 appeared to be a satisfactory precursor to

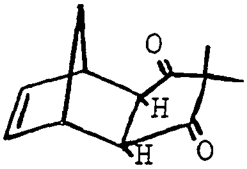


65

study long-range interactions of a 1,4 spin label. The Diels Alder adduct of 51 with cyclopentadiene could be separated by column chromatography to the endo (66a) and exo (66b) isomers (3:1).

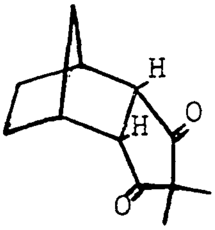


66a



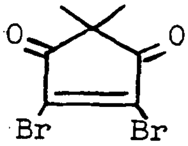
66b

Hydrogenation of 66a gave 67. The hydrogens alpha to the



67

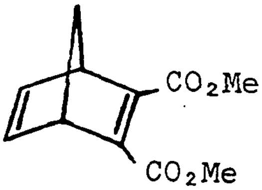
carbonyl in 67 were found to be exchangable in DMSO-d_6 in the presence of potassium t-butoxide. The corresponding alpha hydrogens in 66a or 66b do not exchange under the same conditions. The introduction of a conjugated double bond in 66 and 67 was attempted by treatment with DDQ or selenium dioxide under a variety of conditions. The reactions were followed by pmr, observing no reaction in any case. The Diels Alder reaction of cyclopentadiene with either the monobromide 58 or the dibromide 68 gave no adduct.



68

Extensive heating led to tars. The double bond of 51 did not add chlorine but when a photochemical chlorination was carried out similarly to the chlorination of maleic anhydride (52), the dimethyl group was attacked along with addition to the double bond with no selectivity shown.

A condensation with ethyl propionate and 69 analogous



69

to that in the formation of dimethylindane dione 61 was carried out. Reaction of the resultant sodium salt with methyl iodide indicated (pmr) methylation had taken place but without ring closure.

When the adduct **66a** or **66b** was treated with potassium *t*-butoxide and oxygen/DMSO, a spectrum (Figure 13) was observed. This was tentatively analyzed as a^H=3.48(1H), 1.90(1H), 0.95(1H), and 0.11(6H)G. This indicates a rearrangement or a condensation of the spin label has taken place. The dihydro adduct **67** when treated as above gave a spectrum with a^H=3.18(1H), 1.92(1H), 1.10(1H) and 0.28(3H)G (Figure 14). The presumed hyperfine splitting from the gem-dimethyl group in the radical from **66** could be due to a nonsymmetrically conjugated double bond in this radical, absent in the dihydro adduct. It was also noted the treatment of **50** with potassium *t*-butoxide/DMSO in the absence of oxygen gives a signal with a^H=4.1(1H) and 1.6(1H)G (Figure 15). When oxygen is introduced **52** is observed.

The heterocyclic analogs of 1,4-semidiones resulting from addition of an electron to substituted maleic anhydrides have been used by Nelsen and Seppanen (33,53) to demonstrate long-range splitting in bicyclic structures. Bicyclic hydrazine cation radicals also show long-range interaction (54). The anhydride precursors of the radical anion mentioned above show a number of synthetic advantages over endiones such as **65**. These Diels Alder adducts containing a conjugated double bond are readily available

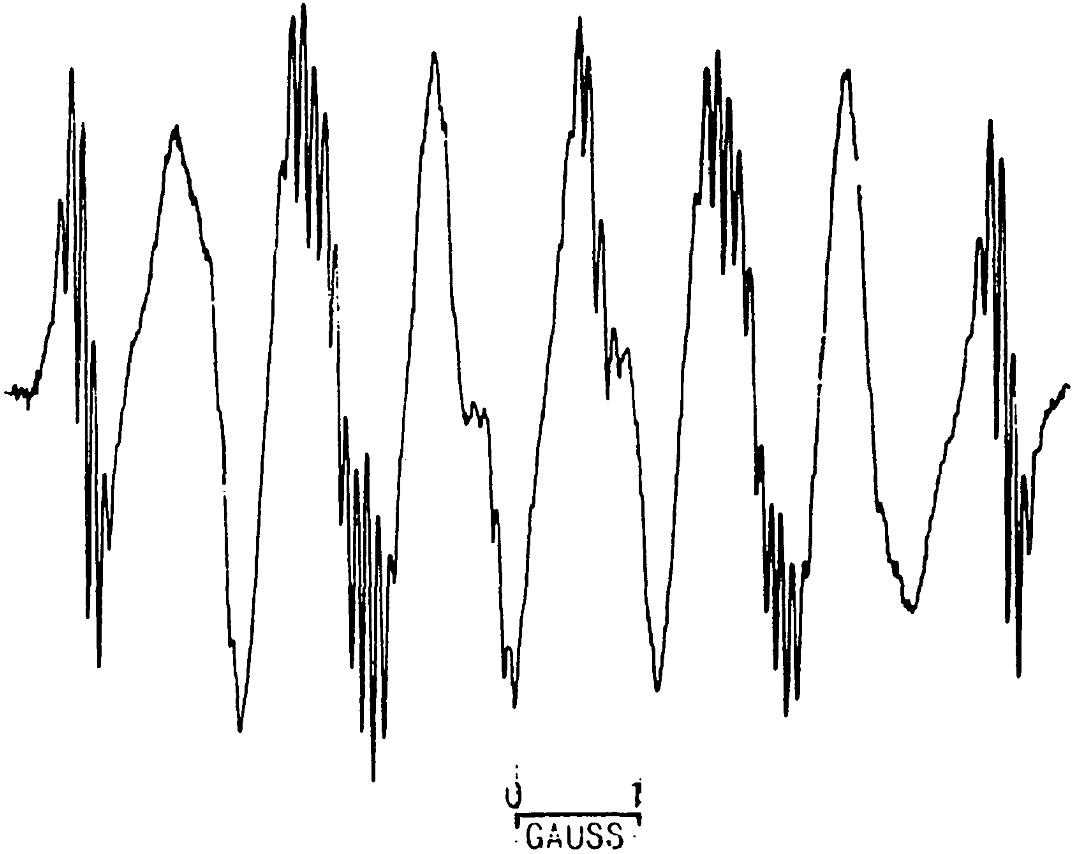


Figure 13. The first derivative esr spectrum of the radical obtained by treatment of 4,4-dimethyltricyclo[5.2.1.$0^{2,6}$]dec-9-ene-3,5-dione (66) with potassium t-butoxide and oxygen in DMSO.

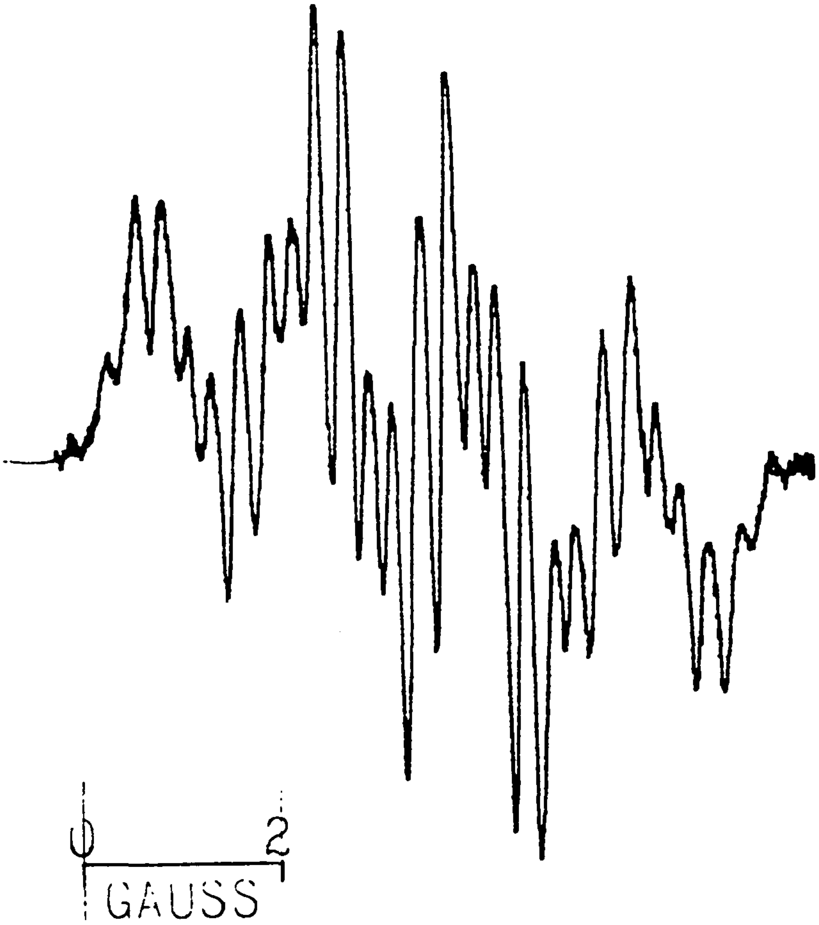


Figure 14. The first derivative esr spectrum of the radical obtained by treatment of endo-4,4-dimethyltricyclo[5.2.1.0^{2,6}]decane-3,5-dione (67) with potassium *t*-butoxide and oxygen in DMSO.

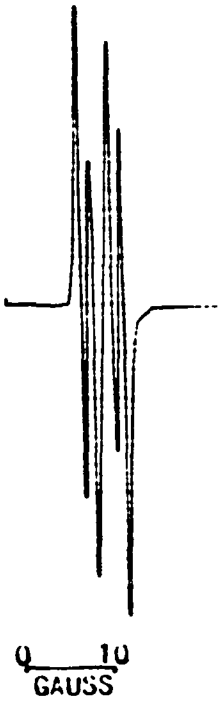
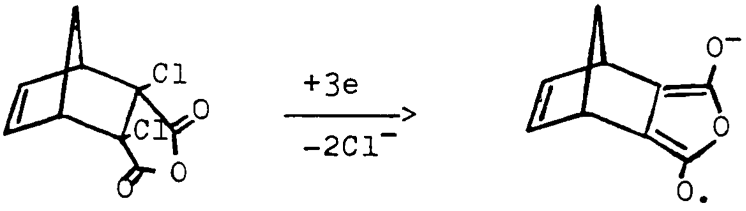


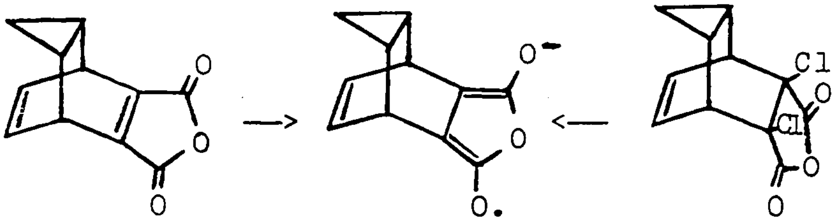
Figure 15. The first derivative esr spectrum obtained by treatment of 2,2-dimethylcyclopentane-1,3-dione (50) with potassium t-butoxide and DMSO in the absence of oxygen.

from a diene and acetylene dicarboxylic acid derivatives, usually the diester. These can be hydrolyzed and cyclized to the anhydride. Ring closures in similar carbocyclic systems are unworkable due to steric effects. Another convenient method of generation of this type of radical is by reaction of dichloromaleic anhydride with a diene. The adduct (eq. 71) can be electrolytically reduced to the radical ion 70 by addition of three electrons with concomitant loss of two chlorides.



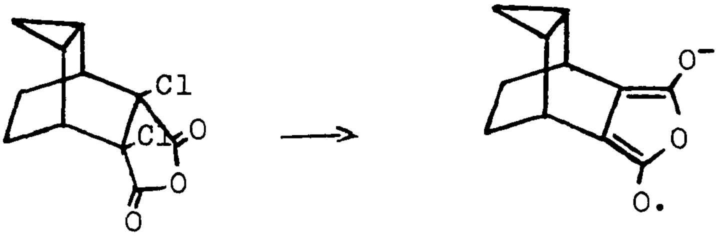
71 70

A sealed tube reaction of cycloheptatriene and dimethyl acetylene dicarboxylate (55) gave an adduct which was hydrolyzed to the diacid and treated with acetic anhydride to give 72. The adduct 74 was formed from cycloheptatriene



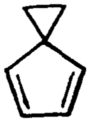
72 73 74

and dichloromaleic anhydride. Electrolytic reduction of either 72 or 74 in DMSO gave 73 (Figure 16), a^H=1.11(2H) and 0.35(1H)G. The latter hfsc was estimated from peak shape. Hydrogenation of 74 gave 75 which was electrolyzed in DMSO to give 76, a^H=1.72(2H), 0.50(2H), 0.19(3H) (Figure 17).



75 76

The reaction of the spirodiene 77 with dichloromaleic anhydride gave 78 which was electrolyzed to give 79 in DMSO, a^H=1.10(2H), 0.82(2H), 0.55(2H), and 0.46(2H)G (Figure 18).



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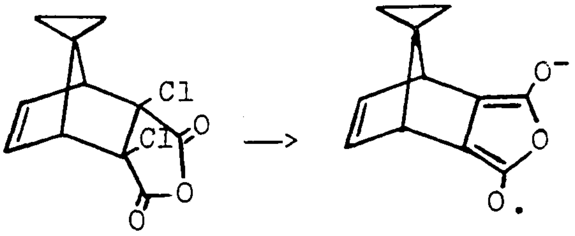


78 79

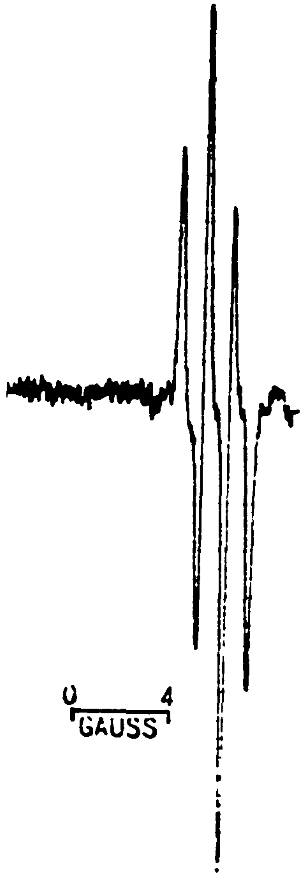
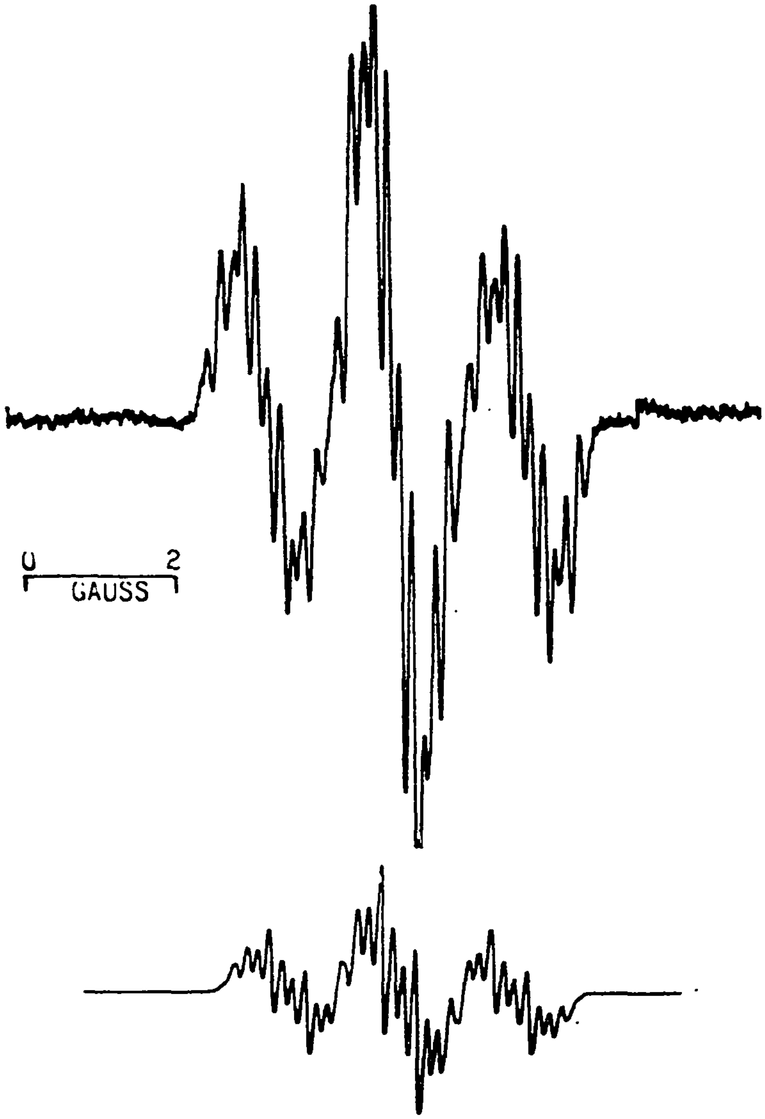


Figure 16. The first derivative esr spectrum of the radical ion 73 from endo-tricyclo[3.2.2.0^{2,4}]-6,9-nonadiene-6,7-dicarboxylic anhydride (72) in DMSO.

Figure 17. The first derivative esr spectrum (top) of the radical anion **76** from 6,7-dichloro-endo-tricyclo[3.2.2.0^{2,4}]nonane-endo-6,7-dicarboxylic anhydride (**75**); calculated spectrum (bottom) for Lorentzian line width 0.20 gauss and splitting constants from text performed by JEOLCO JMN-RA-1 spectrum accumulator.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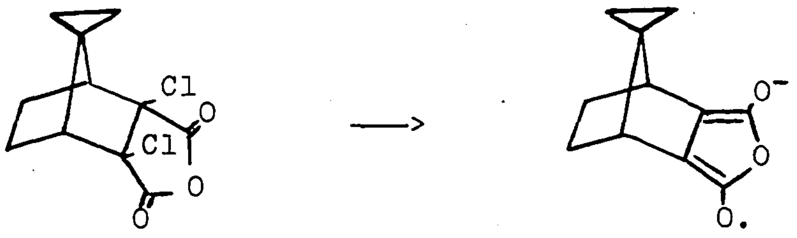
Hydrogenation of 78 gave 80 which produced 81 upon electrolysis, $\underline{a}^{H}$=2.10(2H), 1.15(2H), 0.46(2H), 0.23(4H)G (Figure 19).

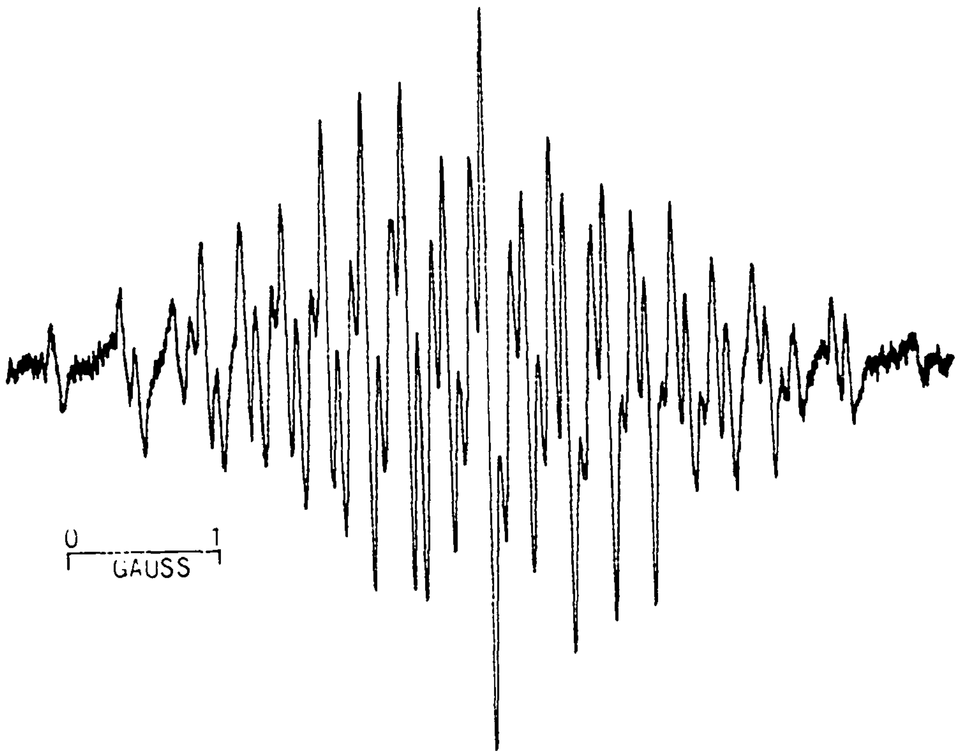


80 81

7,7-Dimethylfulvene added to dichloromaleic anhydride to give 82 which was electrolyzed in DMSO to give 83, $\underline{a}^{H}$=0.98(2H), 0.34(2H), 0.15(6H)G (Figure 20). The anhydride

82 83

Figure 18. The first derivative esr spectrum (top) of the radical ion **79** from 2,3-dichloro-1,2,3,4-tetrahydro-1,4-(1,1-cyclopropano)-phthalic anhydride (**78**) in DMSO; calculated spectrum (bottom) for Lorentzian line width 0.06 gauss and splitting constants from text performed by JEOLCO JNM-RA-1 spectrum accumulator.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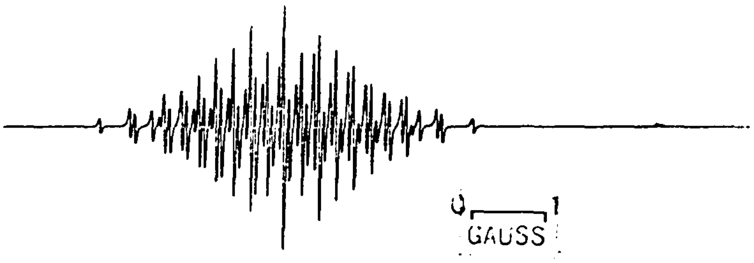
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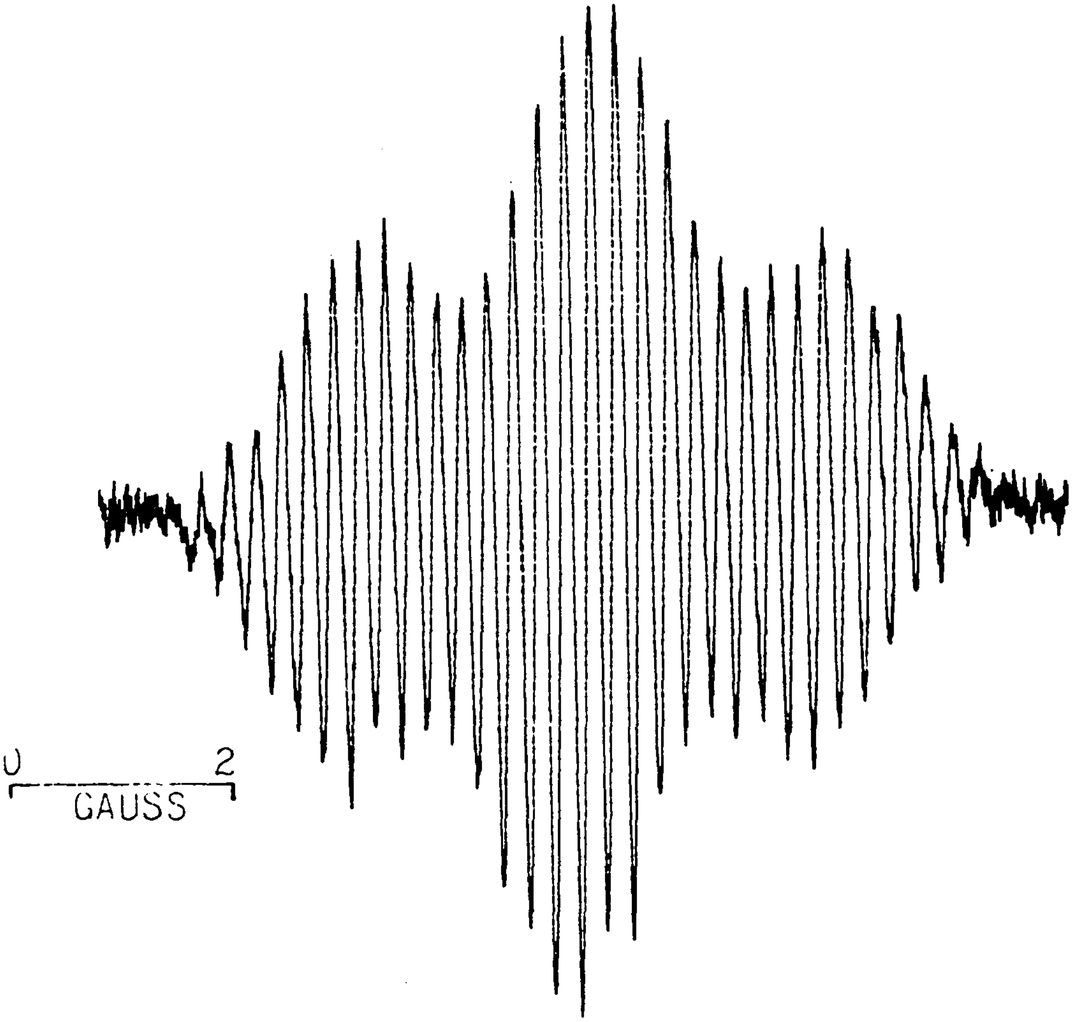
Figure 19. The first derivative esr spectrum (top) of the radical ion 81 from 1,2-dichloro-3,6-(1,1-cyclopropano)-cyclohexane-1,2-dicarboxylic anhydride (80) in DMSO; calculated spectrum (bottom) for Lorentzian line width 0.2 gauss and splitting constants from text performed by JEOLCO JNM-RA-1 spectrum accumulator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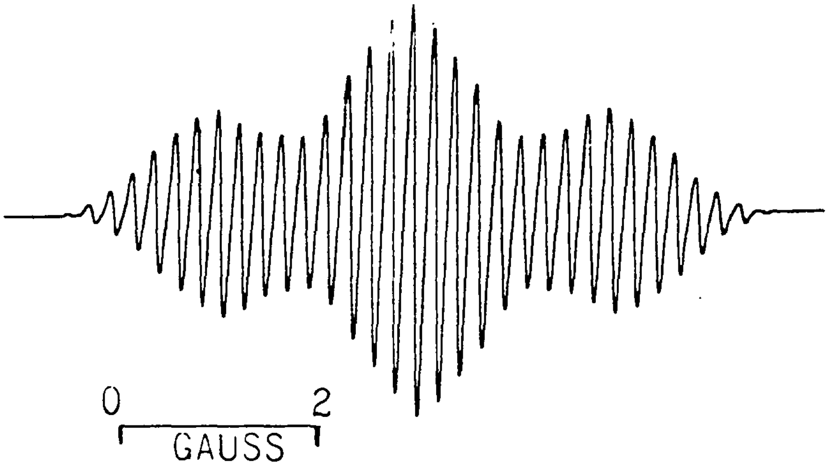
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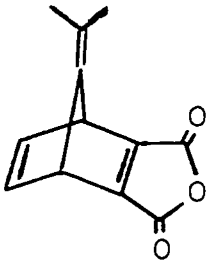
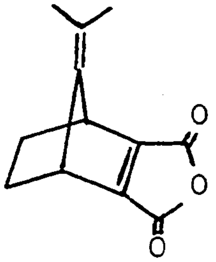
84 upon electrolysis gave a spectrum (Figure 21) with $\underline{a}^{H}$= 1.41(1H), 0.80(1H), 0.62(2H), and 0.16(6H)G. This is not consistent with 83. The dihydro adduct 85 was reduced under

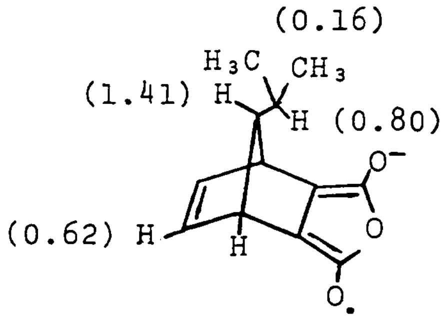


84



85

the same conditions to give a radical with $\underline{a}^{H}$=2.29(2H), 0.79(1H), 0.66(2H), 0.46(2H), 0.17(2H)G (Figure 22). The reduction of 84 and 85 obviously did not yield the expected radical anions. Structures 86 and 87 seem to be consistent



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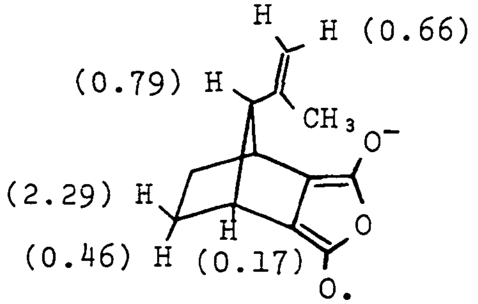
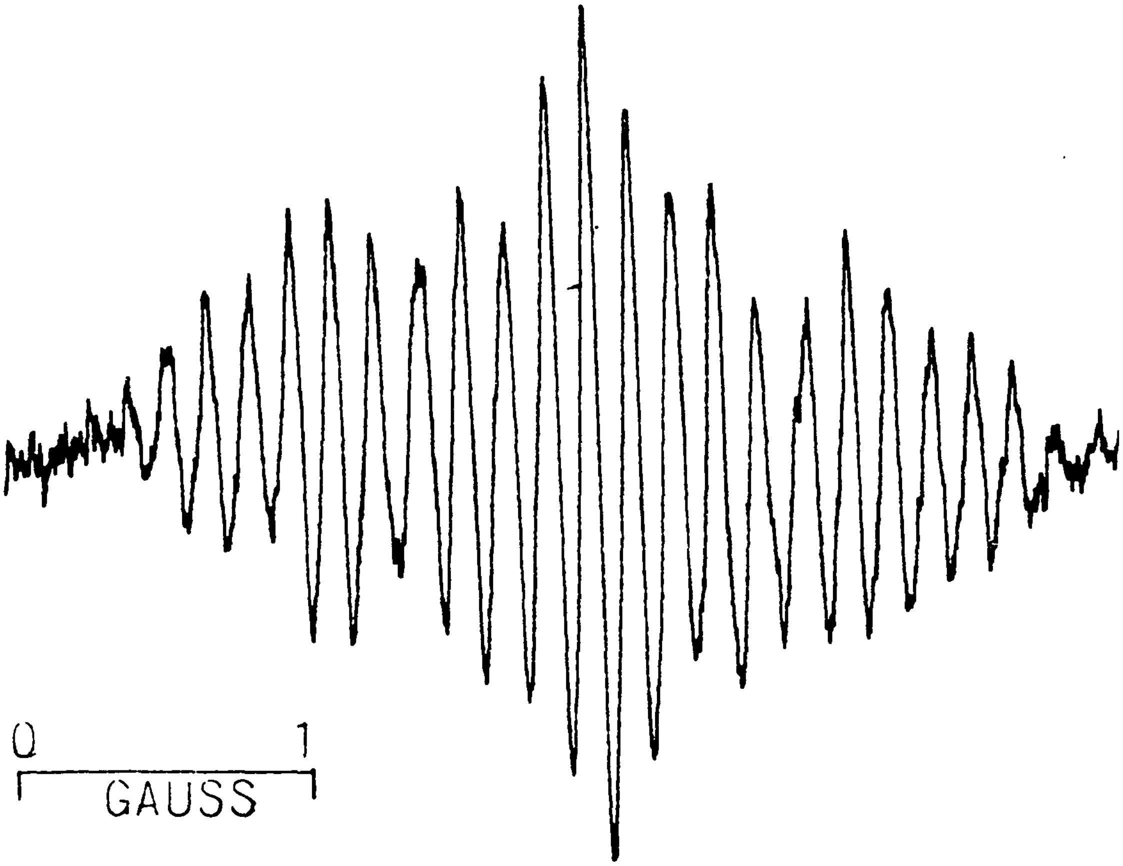


87

Figure 20. The first derivative esr spectrum (top) of the radical ion 83 from 2,3-dichloro-7-isopropylidinebicyclo[2.2.1]-5-heptene-2,3-dicarboxylic anhydride (82) in DMSO; calculated spectrum (bottom) for Lorentzian line width 0.4 gauss and splitting constants from text performed by JEOLCO JNM-RA-1 spectrum accumulator.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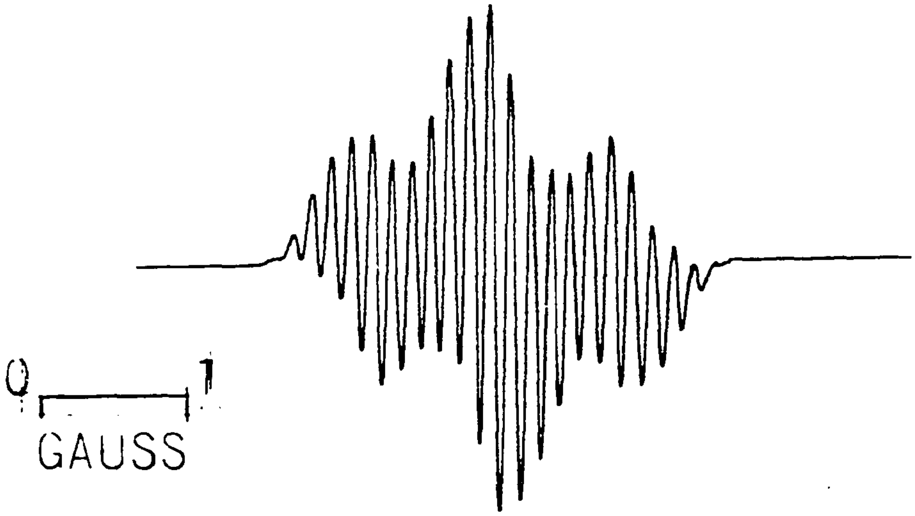
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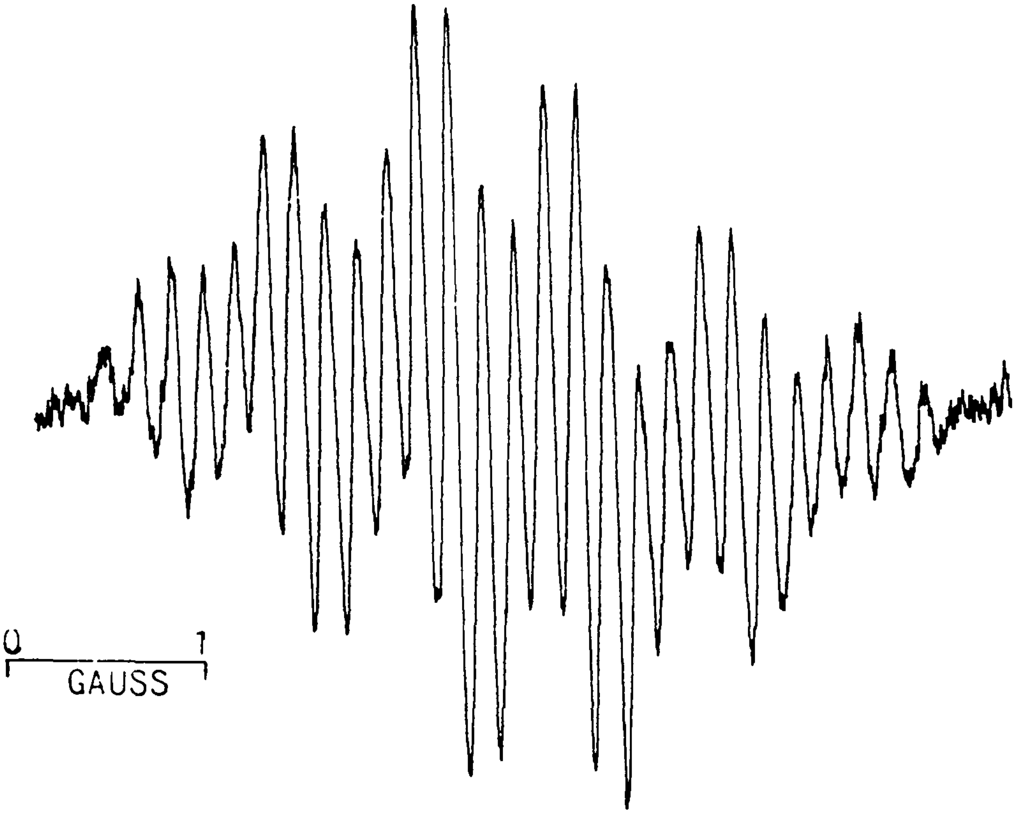
Figure 21. The first derivative esr spectrum (top) of the radical ion 86 from 7-isopropylidinebicyclo[2.2.1]-2,5-heptadiene-2,3-dicarboxylic anhydride (84) in DMSO; calculated spectrum (bottom) for Lorentzian line width 0.3 gauss and splitting constants from text performed by JEOLCO JNM-RA-1 spectrum accumulator.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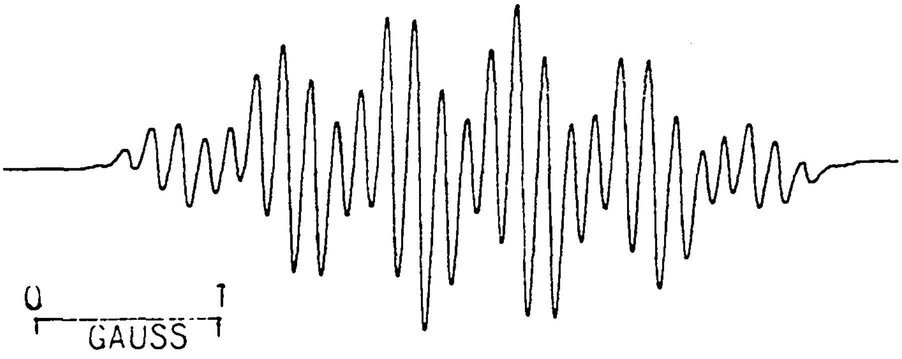
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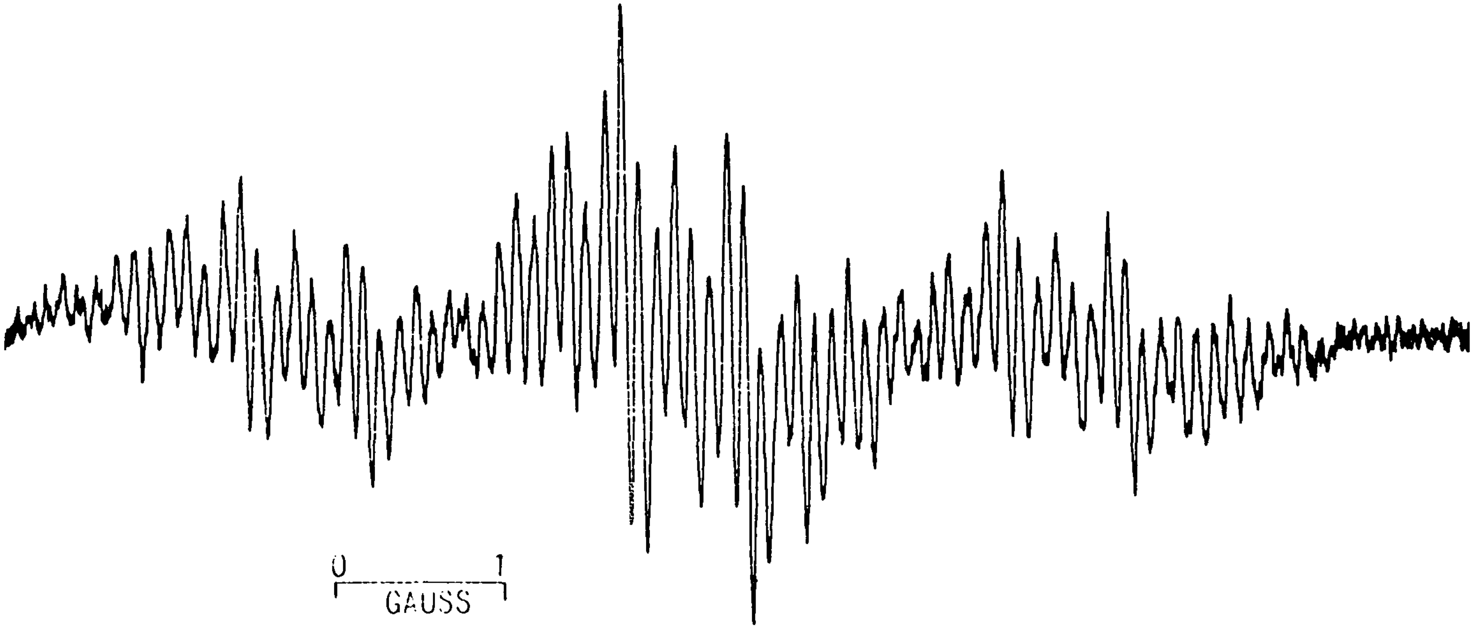
Figure 22. The first derivative esr spectrum (top) of the radical ion **87** from 7-isopropylidinebicyclo-[2.2.1]-2-heptene-2,3-dicarboxylic anhydride (**85**) in DMSO; calculated spectrum (bottom) for Lorentzian line width 0.06 gauss and splitting constants from text performed by JEOLCO JNM-RA-1 spectrum accumulator.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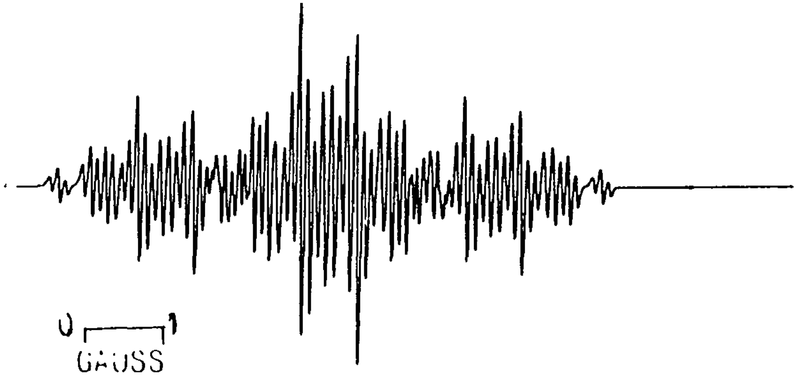
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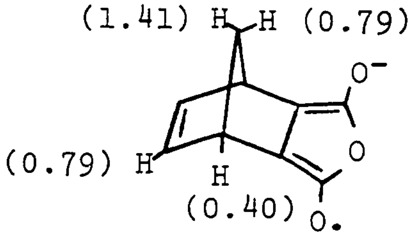
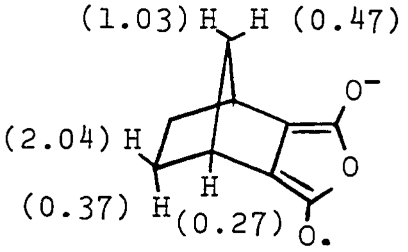
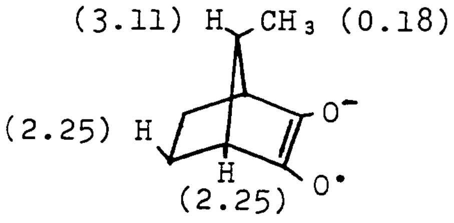
with the observed hfscs. The assignment of hfscs are based upon analogy with known [2.2.1] bicyclic radical ions 70 and 88-90.



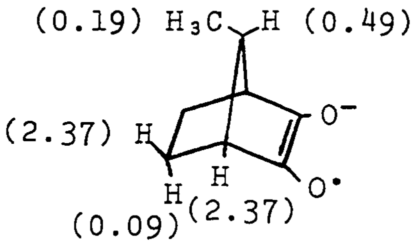
70 (33)



88 (33)

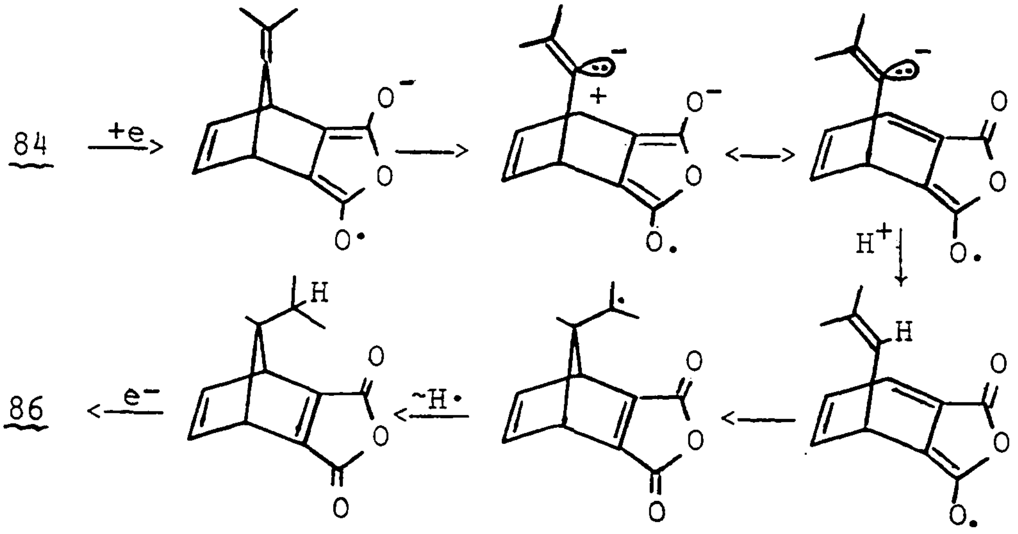


89 (56)

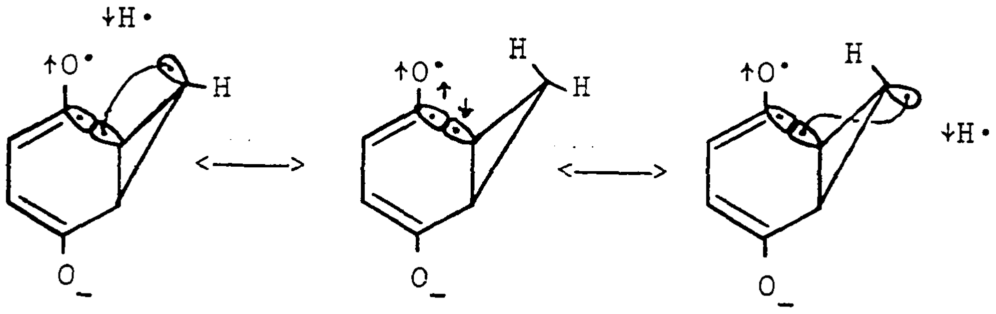


90 (56)

The reduction potentials required to observe radical ions for 84 or 85 were considerably higher (10v vs. 3v applied) than for other conjugated anhydrides such as 72. It appears the presence of the isopropylidine group significantly raises the reduction potential of the maleic anhydride moiety. Whatever the nature of the interaction, the addition of the electron at high potential leads to further chemical change. A rationalization for the formation of 86 is shown below.



The preceding data along with other examples from the literature may be used to rationalize a general mechanism for long-range spin interaction. The data to be discussed can be best explained by two mechanisms operating concurrently. As noted, spin polarization can impart spin of opposite sign on the interacting atom, while hyperconjugation (or homohyperconjugation) maintains spin sign. This results in the possibility of a cancellation when both mechanisms are operating. By proper choice of molecular geometry and spin label symmetry it is possible to differentiate situations where both or only one of these mechanisms is operational. A pertinent example is that of 91 (23) where the spin label has unpaired spin in ψ_4 and the cyclopropyl methylene is in the nodal plane negating any spin contribution from delocalization of spin in the π molecular orbital (homohyperconjugation). The mechanism for introduction of spin into the sigma bond by spin polarization without electron transfer is shown below. This may be visualized in several ways, the most straight forward is polarization of the sigma bond adjacent to a trigonal atom of the spin label and allowing this to interact with the methylene hydrogens by hyperconjugation. A small directional effect is noticed.

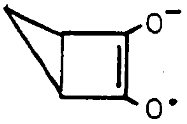


$a^{H}_{syn} = 0.75G$

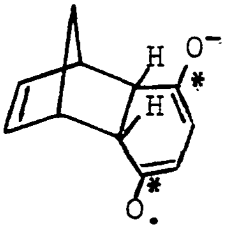
$a^{H}_{anti} = 1.65G$

91

The 1,2 spin label of comparable structure (92) is unknown. In choosing models for comparison it is desirable to have identical geometries and similar spin densities in each radical at the adjacent (starred) trigonal atoms. The known radicals 93 (57) and 94 (58) differ in both of these respects. A proper choice of structures for comparison would be 70 and 95. However, precursors of 95 such as the benzoxy ketone 96 have been found to rearrange to the bicyclo[3.2.0]



92



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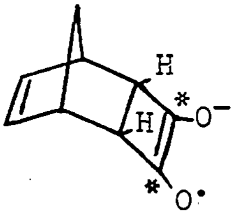

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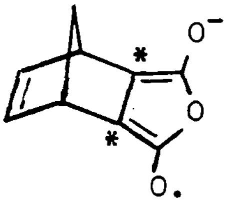

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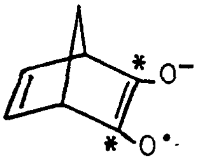

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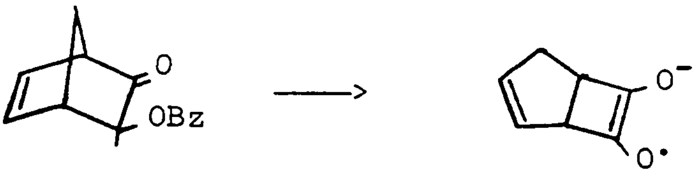
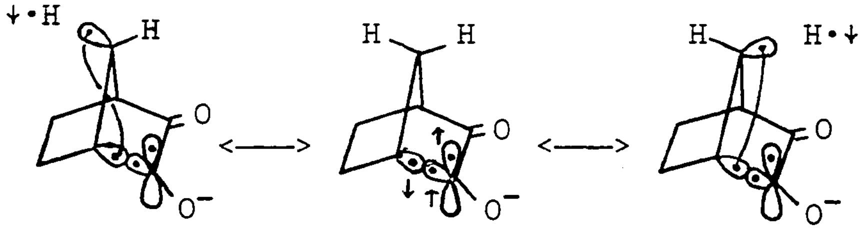


96

97

radical ion 97 when treated with base in DMSO (59). Radical ion 76 is among a series of structures differing in spin label listed in Table 2, and suitable for comparison of symmetry effects. The anion radicals are listed in order of increasing length of the upper bridge: one carbon → double bond → cyclopropyl → single bond. Admittedly, the first and second differ a larger amount than the others.

The hydrogen atoms in the nodal plane of ψ_4 in 88 and 76 could derive spin density by a spin polarization mechanism similar to 92.



88

The a^H_{anti}/a^H_{syn} ratio (1.03/0.47 = 2.2) is the same as that of 91 (1.65/0.75 = 2.2). The nodal hydrogen of 76 is small because spin polarization falls off rapidly with distance. The 2.2 ratio in favor of the trans hydrogen which is in a favorable position for hyperconjugation, may still be valid. The a^H_{anti} = 0.08G necessary to maintain this ratio is near the limit of resolution for this radical solution.

If the unpaired spin is in a symmetric MO as in 98, a strong $(c_1+c_2)^2$ electron delocalization can take place.

Table 2. Comparison of long range splitting from spin labels of different symmetry

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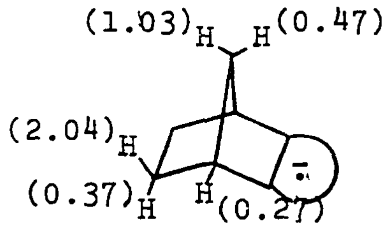
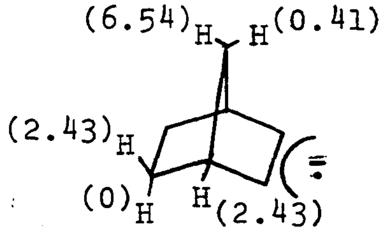
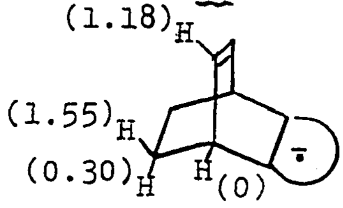


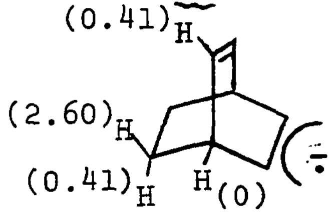
88 (33)



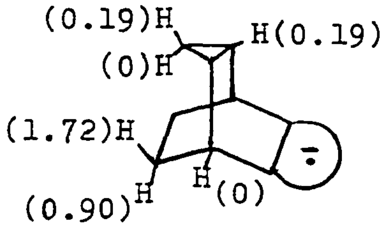
98 (60)



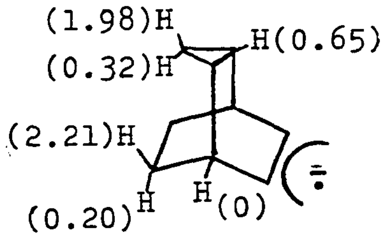
99 (33)



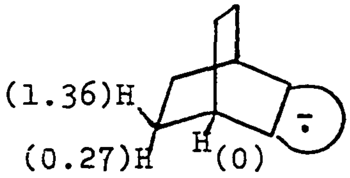
100 (25)



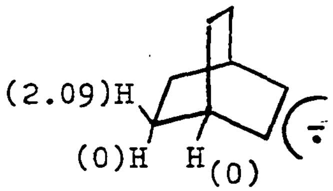
76



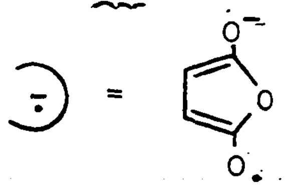
101 (56)

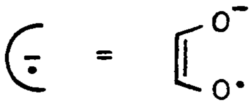


102 (33)

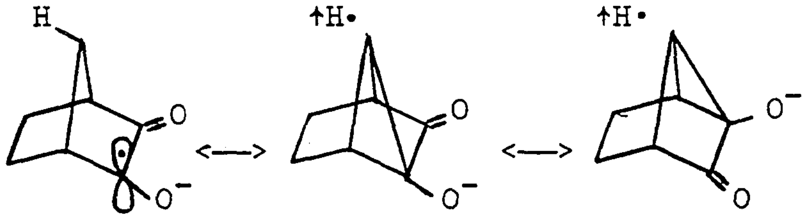


103 (60)





This is most probably a through-bond interaction, strongly favoring those atoms in a zig-zag coplanar arrangement. This is most easily visualized for atoms beta to the spin label by a homohyperconjugation mechanism.



98

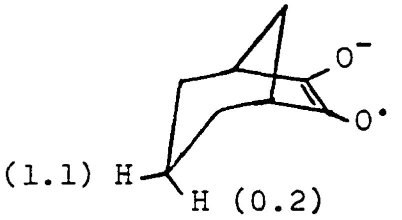
This takes place concurrently with and is dominant over spin polarization, a $\rho_1+\rho_2$ function. The *syn* hydrogen cannot interact by backside bonding, but a reverse spin polarization might be envisioned allowing it to acquire positive spin density. Alternatively, this explanation is not needed stated in terms of a through-bond interaction with directional selectivity.

The a^{H}_{anti} in 98 is necessarily positive, but a^{H}_{syn} could either be positive or a decreased negative value depending upon the extent of hyperconjugation. Preliminary calculations[2] indicate the spin density is positive for both the *syn* and *anti* hydrogens under consideration. Spin

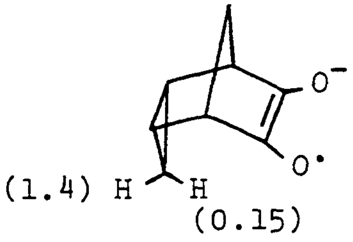
---

[2] C. Chung, Iowa State University, Ames, Iowa. Private Communication (1973). All valence electron semiempirical SCF MO calculation of the INDO type.

polarization is a function of the spin densities of the directly interacting trigonal carbons in the spin labels and is assumed constant for molecules differing only in (1,2 vs. 1,4-) spin labels. This is reasonable since although HOMO symmetry changes, the variation in geometry and trigonal spin density is small. Therefore, the hfscs that would be observed in **98** if homohyperconjugation alone were operational are $a^{H}_{\underline{anti}}/a^{H}_{\underline{syn}} = 7.5/0.9 \cong 8$, assuming a positive *syn* hfsc. This is in good agreement with **101** corrected for spin polarization (76), $a^{H}_{\underline{syn}}/a^{H}_{\underline{anti}} = 2.2/0.32 \cong 7$. The spin polarization contributions to the hydrogens shown in **104** and **105** (20) would be small indicating an *anti*/*syn* ratio in this order of magnitude is maintained.



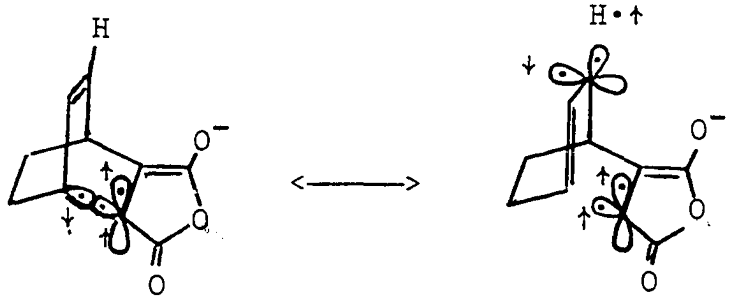
104



105

If the $a^{H}_{\underline{syn}}$ in **98** were negative the homohyperconjugation contribution to the hfscs would be $7.5/0.06 \cong 100$.

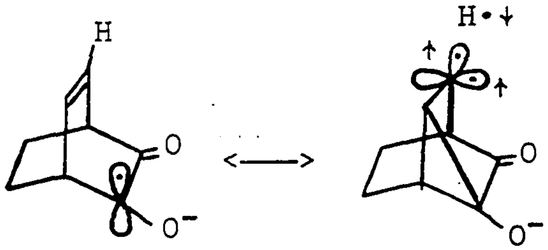
The hfsc of the vinyl hydrogens in 99 can result from polarization of the sigma framework. The HOMO (ψ_4) is antisymmetric with respect to the molecular mirror plane and direct interaction with ψ_1(S) of ethylene would be small.



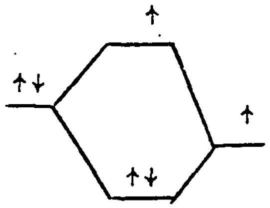
99

The positive spin at the hydrogen shown is in line with the calculated sign[3].

In 100 the HOMO (ψ_3) is symmetric and homoallylic conjugation becomes important.



100



ψ_1 of C=C

ψ_3 of spin label

---

[3] *Ibid*.

Again in 100, both mechanisms may operate and the magnitude of the contribution from direct spin transfer cannot be calculated unless the sign of the spin density on hydrogen is known [*i.e.*, -1.59G, (-0.41-(+1.18)) or -0.77G (+0.41-(+1.18))]. Calculations[4] indicate a negative spin at the vinylic hydrogen of 100 and by this criteria the homoallylic interaction is -1.59G.

The analysis of hfscs from the *syn* and *anti* hydrogens of the two carbon bridge of 88, 98 and 102, 103 is not so straight forward. Both spin interaction mechanisms may operate with spin labels of each symmetry; *i.e.*, the hydrogen does not lie in a nodal plane. Yet, differences exist in the hfscs.

Considering the [2.2.2] structures 102 and 103, a^{H}_{anti} varies from +2.09G → ±1.36G going from a 1,2- to 1,4-spin label. If spin polarization is assumed constant, the charge is due to a lessening of the homohyperconjugation contribution going from 103 → 102. The possibility of $a^{H}_{anti} = -2.09G$ in 103 coming from a spin polarization contribution $>>|-2.09G|$ is out of line for the observed magnitudes of this type interaction. The sign of a^{H}_{anti} in 102 is taken as positive which will later be justified. This would indicate that a^{H}_{syn} goes from 0.0 →-0.27G as homohyperconjugation decreases.

---

[4] *Ibid.*

The contributions to $\underline{a}^{H}$ might be envisioned as arising from: 1) direct homohyperconjugation to the adjacent spin center (H^{A}), 2) a weaker interaction to the other spin site (H^{T}), either a through-bond or transannular 1,3 interaction, and 3) a spin polarization term (S), constant in both cases. The total hyperconjugative contribution would be additive in a 1,2-spin label. With the 1,4-spin label a partial cancellation would result, the limiting situation being when $H^{A}=H^{T}$ (an atom in the nodal plane). If the following assumptions are made, the relative contributions of the three factors can be estimated: 1) that $\underline{a}^{H}_{\underline{anti}}/\underline{a}^{H}_{\underline{syn}} = 2$ for the spin polarization contribution (as observed experimentally for 88 and 91), and 2) $\underline{a}^{H}_{\underline{anti}}/\underline{a}^{H}_{\underline{syn}} = 8$ for the hyperconjugative contribution from the adjacent spin site. The subscript A refers to the *anti* hydrogen and S, the *syn*.

$$H^{A}_{A} = 8H^{A}_{S}$$

$$S_{A} = 2S_{S}$$

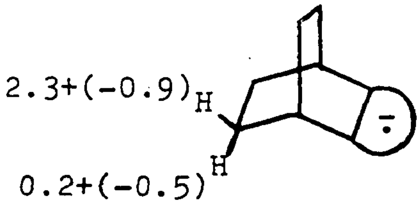
$$H^{A}_{A} + H^{T}_{A} + S_{A} = 2.09$$

$$H^{A}_{A} - H^{T}_{A} + S_{A} = 1.38$$

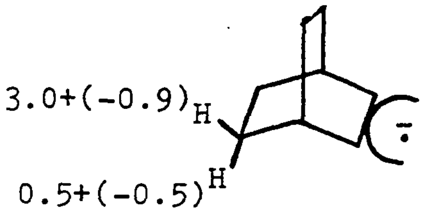
$$H^{A}_{S} + H^{T}_{S} + S_{S} = 0.0$$

$$H^{A}_{S} - H^{T}_{S} + S_{S} = -0.27$$

The solution gives H_A^A = 2.63, H_S^A = 0.32, H_A^T = 0.36, H_S^T = 0.13, S_A = -0.90, and S_S = -0.45G. The estimated homohyperconjugation (+) and spin polarization (-) contributions to the observed hfscs are listed below.



102



103

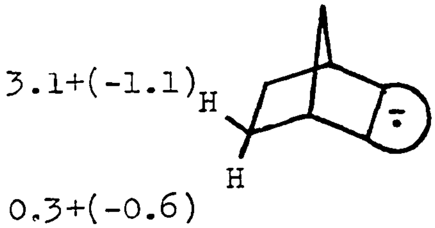
If $a_{\underline{anti}}^H$ in 102 was taken as -1.38G and the calculation repeated, H_A^A = 0.6G and H_A^T = 1.7G which is unlikely.

A similar analysis of 88 and 98 gives

H_A^A = 3.33G H_S^A = 0.42G

H_A^T = 0.19G H_S^T = 0.13G

S_A = -1.09G S_S = -0.55G



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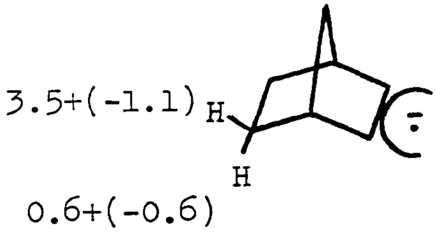
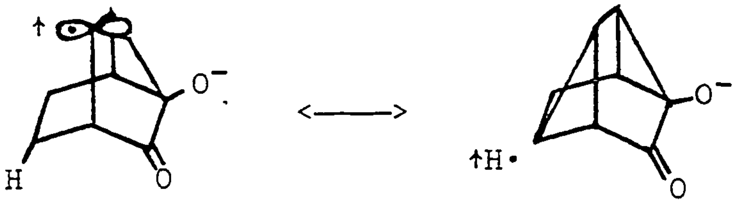


98

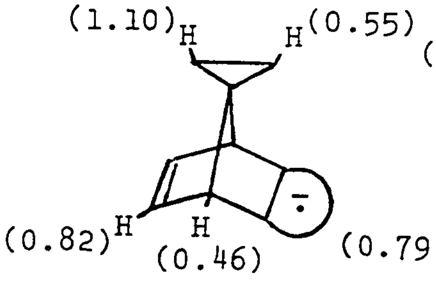
More examples are needed to more accurately estimate H_A^A/H_S^T, and its variation with structure. Perhaps $(H_A^A+H_A^T)/(H_S^A+H_S^T)$ is significant although this ratio is difficult to get at experimentally.

If the bridge methylene hydrogens are considered for 99 and 100 and compared to the corresponding positions in 88 and 102 (for 99) and 98 and 103 (for 100), the magnitudes of these hydrogens in 99 seem intermediate and might be ascribed to a geometric change. In 100 the variation can be attributed to interactions with spin density in the ethylene double bond.



100

The assignments of hfscs to hydrogens in 79 and 81 are possible if it is assumed that the $a^{H}_{\textit{anti}}/a^{H}_{\textit{syn}}$ are similar to 79 and 88 respectively.



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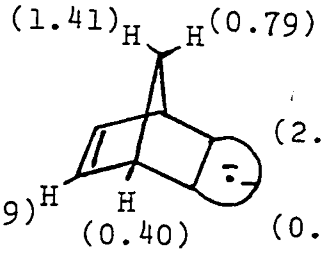

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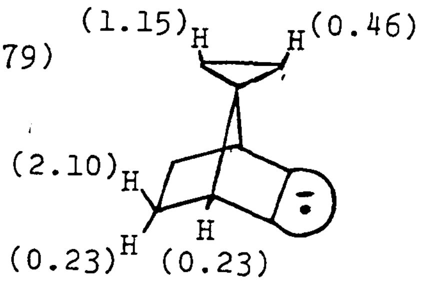
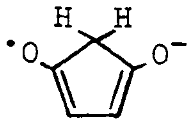


81

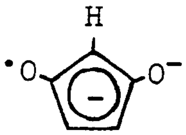
The hfscs for the cyclopropyl hydrogens are larger than expected. This perhaps reflects increased strain in the carbocyclic system.

1,4 Semidiones with Acidic Hydrogens

If a radical ion (106) is generated from 4-cyclopentene-1,3-dione (unsubstituted 51), it might be expected

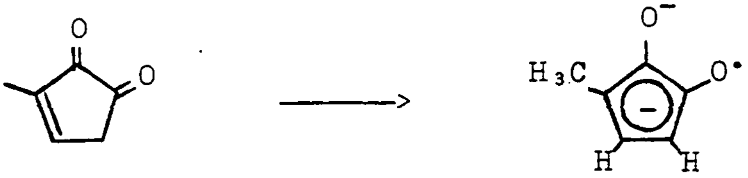


106



107

to lose a proton to yield the dianion radical 107 because of stabilization of nonbenzenoid aromaticity. A similar phenomenon was observed in an unsaturated 1,2 semidione 108.



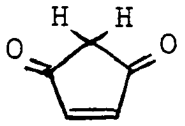
108 109

Selenium dioxide oxidation of the corresponding enone gave 108 (61). Electrolytic reduction in DMF gave a radical with a^H = 6.3(H) and 0.85(5H)G (Figure 23). Calculated

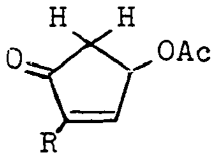
Figure 23. The first derivative esr spectrum of the dianion radical 109 produced from 3-methyl-3-cyclopentene-1,2-dione (108).

values with Q^{H}_{CH} = 24 and $Q^{H}_{CH_3}$ = 20 are a^{H} = 7.6(1H), 1.9(1H) and 1.6(3H).

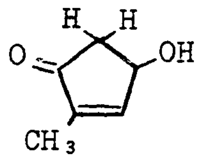
Treatment of 110 with potassium t-butoxide/DMSO under



110

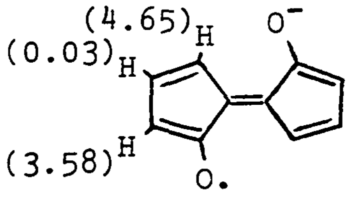


111a R=H
111b R-CH_3

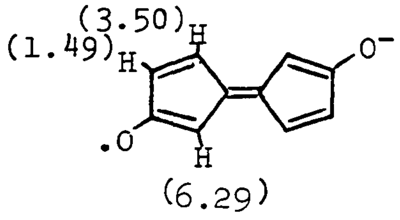


112

flow conditions gave no esr signal. A large amount of insoluble material was found. The enones 111 and 112 appeared to be less sensitive to basic polymerization than 110 and it was felt that a radical formation process vinylogous to that of acetoxy or hydroxy ketones might compete favorably. Treatment of 111a with potassium t-butoxide gave no signal but introduction of oxygen allowed observation of a radical, a^{H} = 3.2(2H), 2.0(2H) and 0.7(2H) (Figure 24). A condensation had evidently taken place. The calculated values are indicated for the two symmetrical dimers 113 and 114 (see Appendix).



113



114

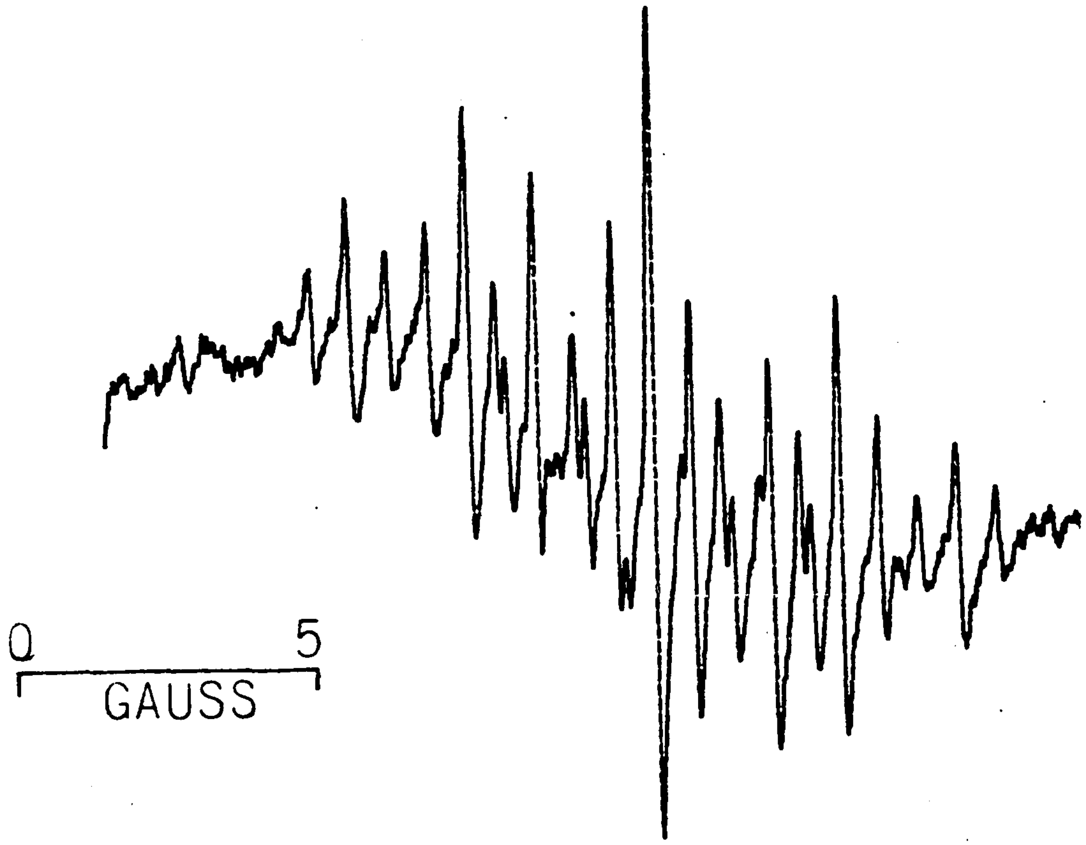
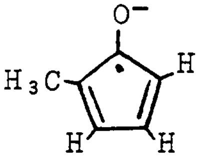


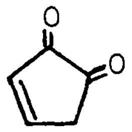
Figure 24. The first derivative esr spectrum of the anion radical produced by treatment of 4-acetoxy-2-cyclopentenone (111a) with potassium *t*-butoxide and oxygen in DMSO

A flow experiment with 111b with base/DMSO gave a_H = 6.3(1H), 4.3(1H), 3.1(3H) and 2.1(1H)G (Figure 25). This radical appears to be the ketyl 115 resulting from loss of acetic acid and addition of an electron. A flow experiment with 112 also gave a spectrum similar to Figure 25.

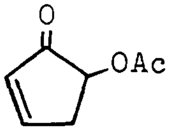


115

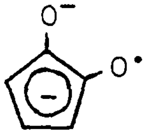
A complex signal was observed when 116 was electrolyzed in DMF. The acetoxy ketone 117 was prepared in an attempt to prepare the dianion radical 118 but when 117 was treated



116



117



118

with potassium t-butoxide in a flow system a weak signal was observed with a^H = 5.3(2H) and 2.9(2H)G. This is cyclopentadieneone ketyl (119) first reported by Russell

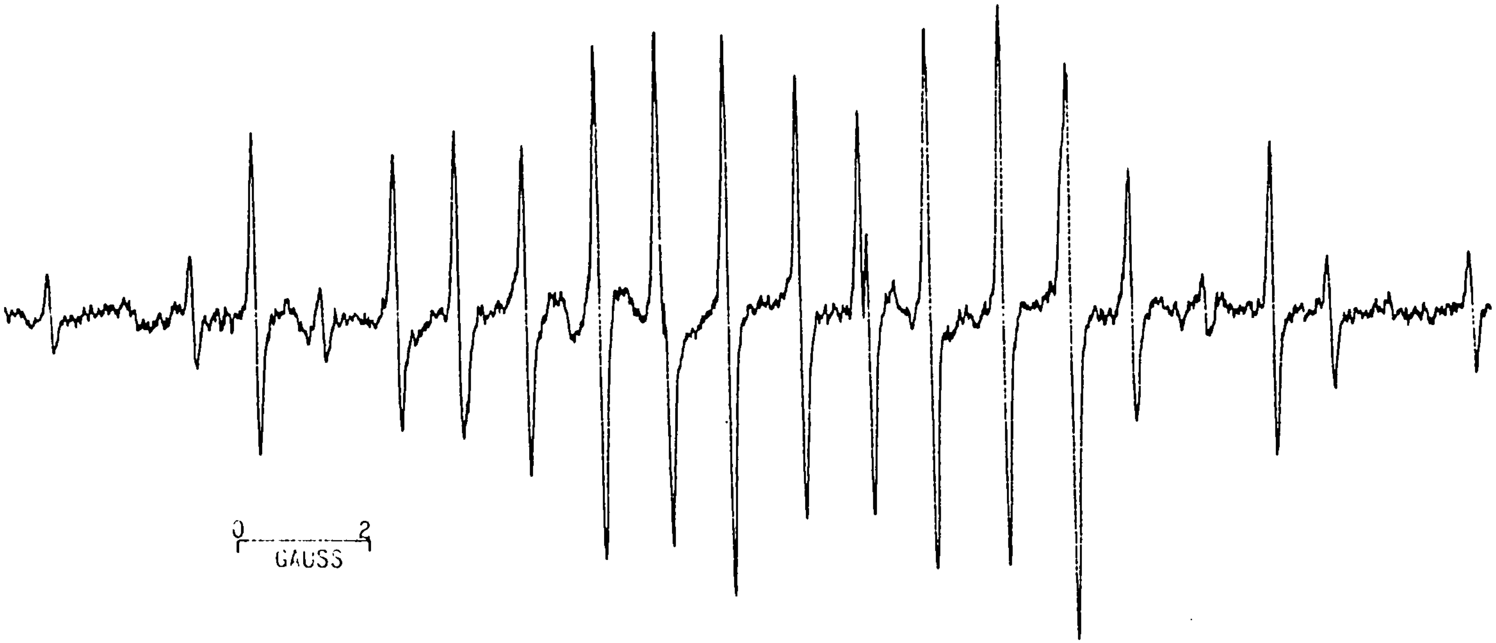
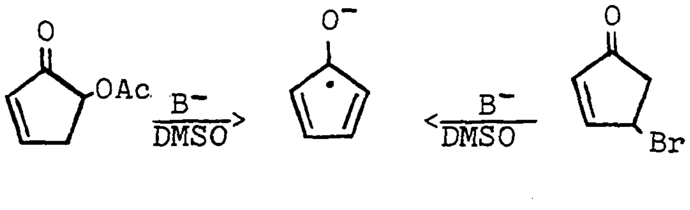


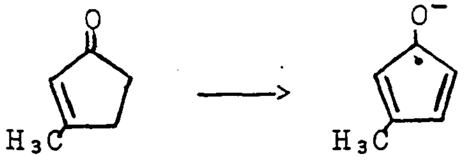
Figure 25. The first derivative esr spectrum of 2-methylcyclopentadienone ketyl (115) in DMSO.

and Blankespoor (34), formed by treatment of 120 with base-DMSO.



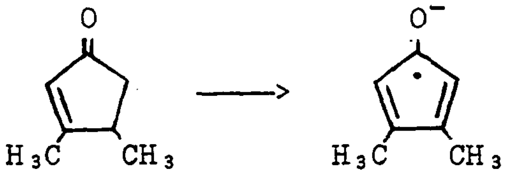
117 119 120

Two other ketyls, 122 (Figure 26) and 124 (Figure 27), were prepared from the corresponding acetoxy ketones 121 and



a^H = 6.2(3H), 5.3(1H), 3.5(1H), 2.5(1H)G

121 122



a^H = 5.9(6H), 2.5(2H)G

123 124

123 by similar flow experiments. If no acidic hydrogen is present (125), an unsaturated 1,2-semidione is observed (126) with a^H = 6.8(3H), 1.2(1H) and 0.5(6H)G (Figure 28).

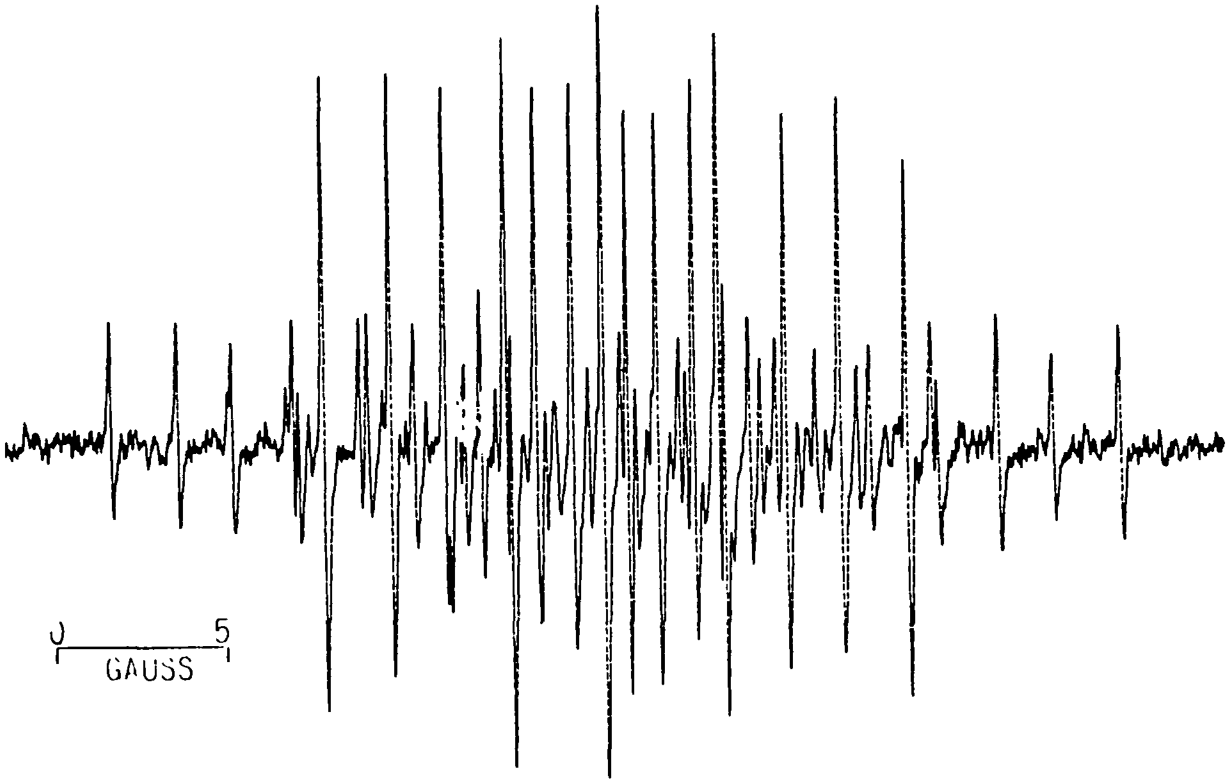


Figure 26. The first derivative esr spectrum of 3-methylcyclopentadieneone ketyl (122) in DMSO.

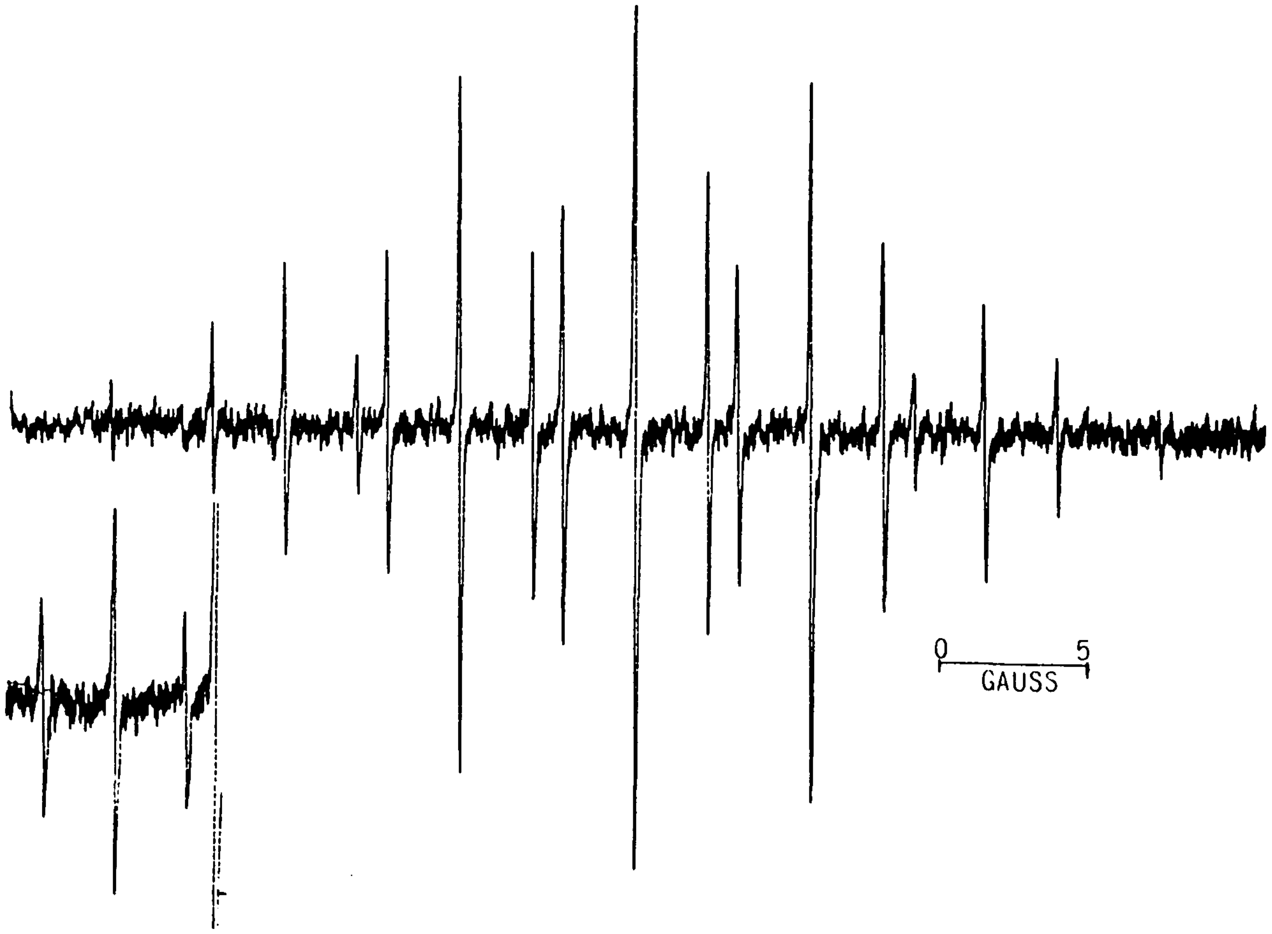


Figure 27. The first derivative esr spectrum of 3,4-dimethylcyclopentadieneone ketyl (124) in DMSO.

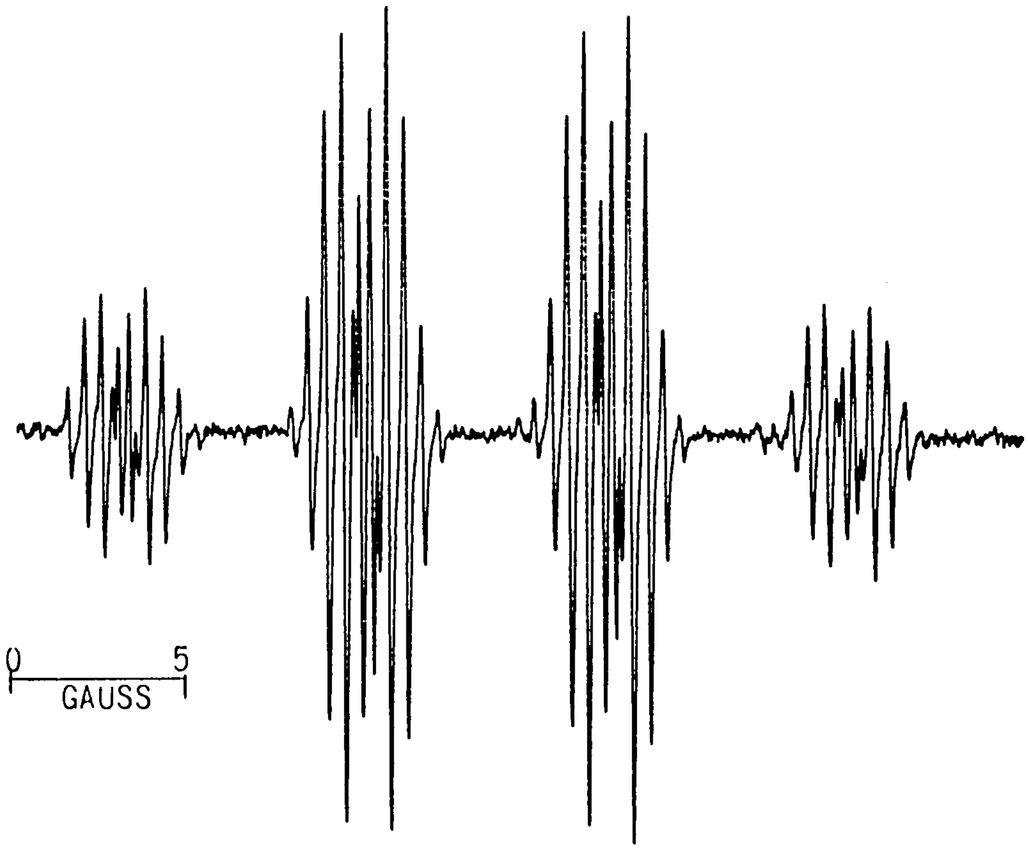
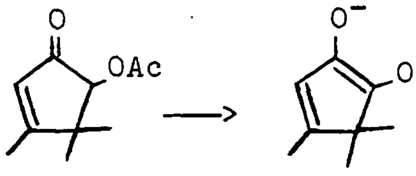
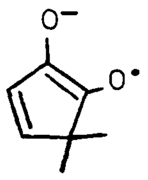


Figure 28. The first derivative esr spectrum of 4,5,5-trimethyl-3-cyclopentene-1,2-semidione (126) in DMSO.

The radical 126 was stable for several hours in contrast to 127[5] reported to be seen under flow conditions only. The

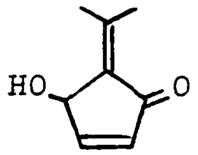


125 126

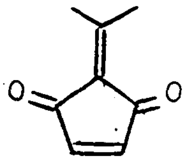


127

hydroxy ketone 128 and dione 129 were prepared (62) by singlet oxygen oxidation of 7,7-dimethylfulvene to give 128 followed by manganese dioxide oxidation to give 129.



128



129

Treatment of 128 with potassium *t*-butoxide/DMSO gave no signal. The 7-methyl hydrogens are vinylogous to the acidic 2-hydrogens of 106 and the instability of their respective anions apparently competes favorably with electron transfer processes.

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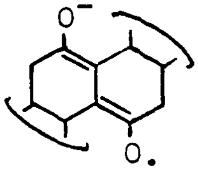
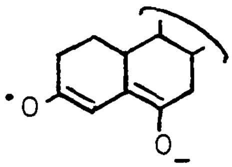
[5] R. Penney, Iowa State University, Ames, Iowa. Private Communication (1971).

1,4 Spin Labels in Two Rings

Examples are known of the 1,4-semidione in two orientations in fused ring systems, trans,trans,trans (130) and cis,trans,trans (131).

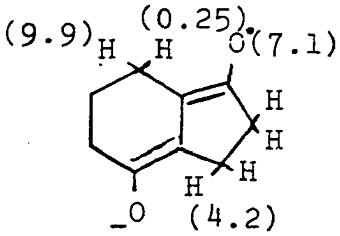


130

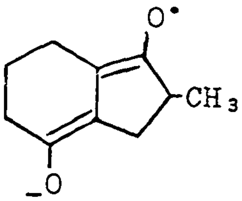


131

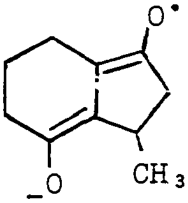
Semidiones of the first type have been observed in the [4.3.0] system (20). The assignments of hfscs of 132 was accomplished by preparing radical ions 133 and 134.



132

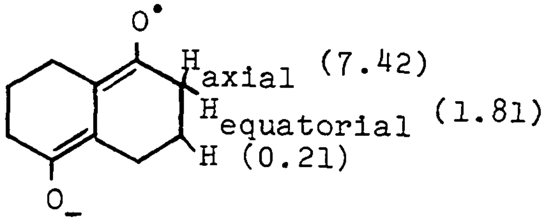


133



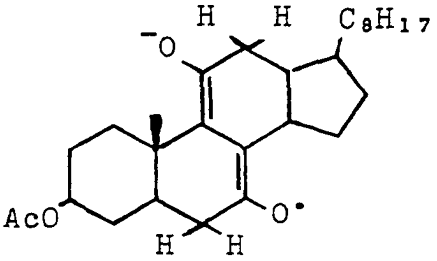
134

The [4.4.0] system 135 gives a spectrum showing line width alternation at room temperature. When cooled to -50° the conformation is frozen, giving three sets of equivalent



135

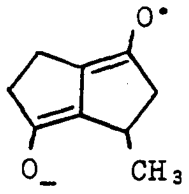
hydrogens (21). Incorporation of the spin label in a rigid steroid gave 136 (19).



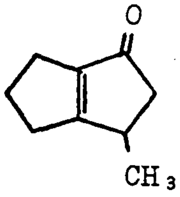
136

a^H = 5.44(1), 4.72(1), 1.38(2)

As a precursor to the [3.3.0] semidione 137, the enone 138 was prepared by polyphosphoric acid condensation of cyclopentyl 2-buteneoate (63).

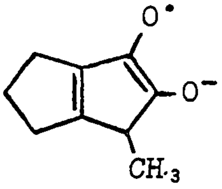


137

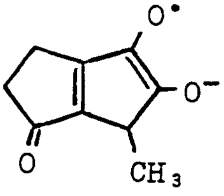


138

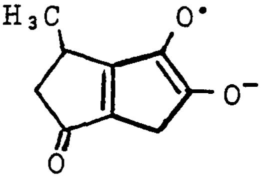
Treatment of 138 with potassium t-butoxide and oxygen in DMSO gave a radical, a^H = 9.0(2H) and 0.22(6H)G (Figure 29). A second, strong esr signal was observed initially but died within the period of one minute. It is suggested that the unstable radical may be 137. Structures 139a,b,c were considered as possible for the more stable oxidation species (see Appendix for calculations). Structures 139b,c



139a



139b



139c

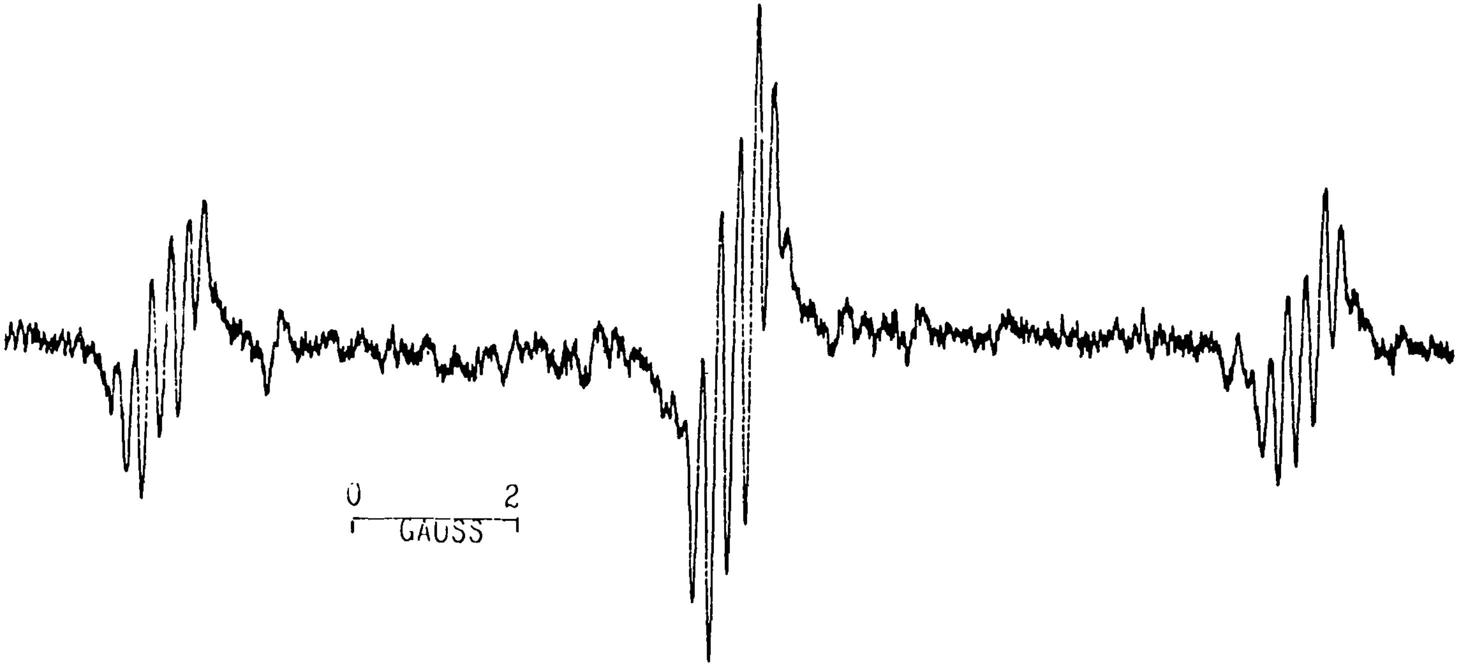
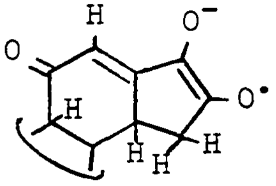


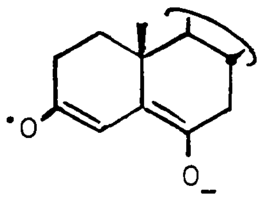
Figure 29. The first derivative esr spectrum of the radical anion obtained by treatment of 4-methylbicyclo[3.3.0]-1-octene-2-one with potassium _t_-butoxide and oxygen in DMSO.

are analogous to the previously reported vinylogous semitrione 140 (19).



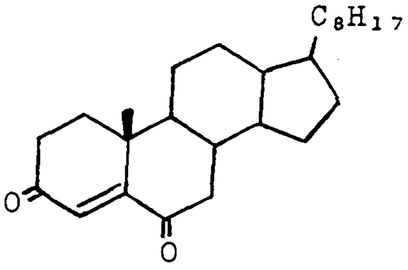
140

The formation of 141 from 5α-cholestane-3,6-dione or its $\Delta^{4,5}$ derivative gave an esr spectrum with broad lines

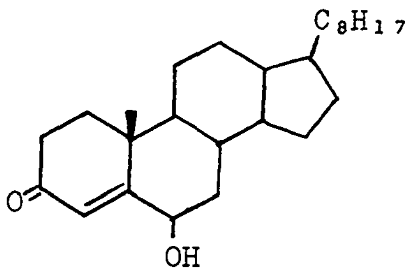


141

interpreted as being the result of a^H = 9.3(1H), 5.2(2H), 2.5(1H), and 1.6(1H)G (19). The radical was produced in low concentration and in order to get a stronger signal a mixture of 142 and 143 was treated with potassium t-butoxide



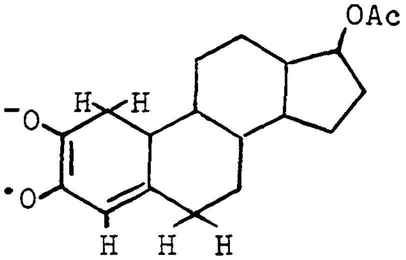
142



143

DMSO in a flow system. Increasing the flow rate materially decreased radical strength until at fast flow no signal was seen. Also, the resolution obtained from the strong signal observed with the mixture of 142 and 143 in a static system was not increased from the weaker signal obtained from 142. alone. These data indicate that the radical formation is slow, unusual for an electron transfer process, and that the poor resolution of the signal is inherent in the nature of the radical solution.

4-Androstae-2β-17β diol-3-one diacetate was reduced with base/DMSO to give 144 (Figure 30).



144

a^H = 12.8(1H), 12.2(1H), 7.1(1H), 5.7(1H)G

The large splittings are assigned to the two axial hydrogens, the equatorial hydrogens being the other two. The lines were somewhat broad and a vinyl hydrogen splitting <0.5G would not have been seen. The hfscs of hydrogen in radical ions derived from rigid steroids are dependent on the geometry in the area of the spin label as observed for

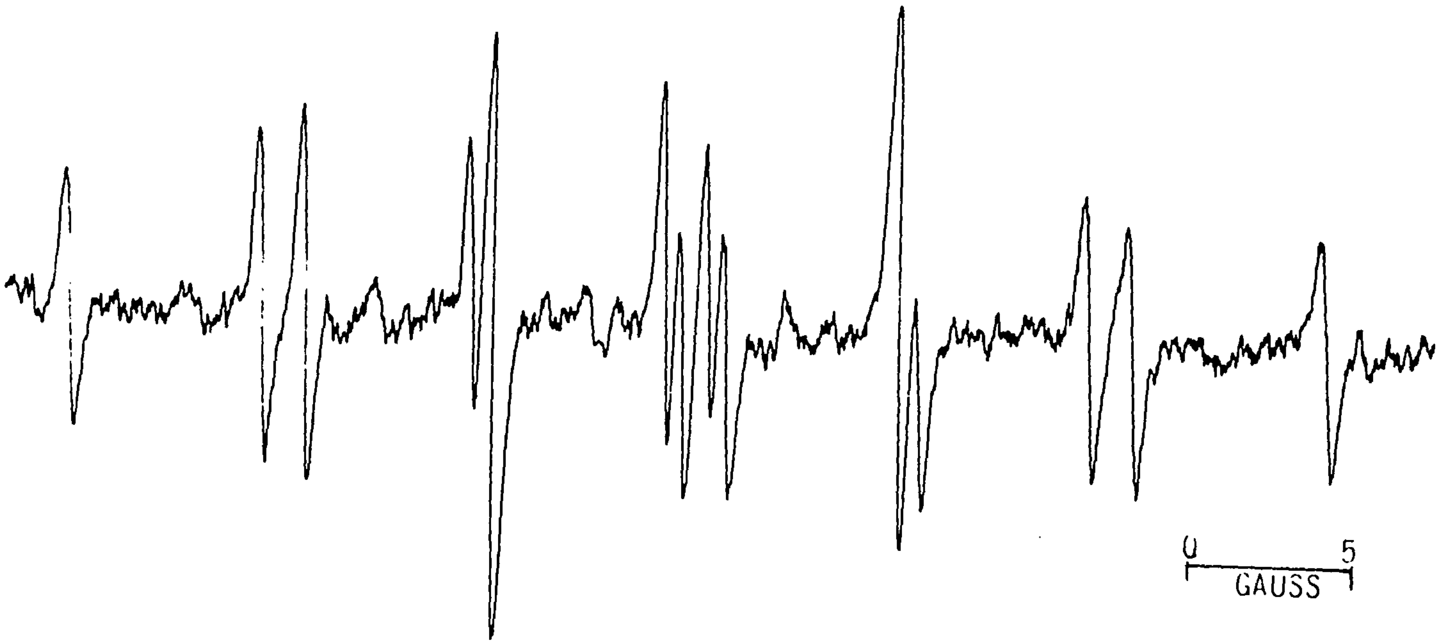


Figure 30. The first derivative esr spectrum of the semidione from 4-androstae-2β,17β-diol-3-one diacetate in DMSO.

the differences in hfscs of 135 and 136. Whether there are inherent differences in the π spin distribution of a cis,trans,trans spin label (144) compared to a trans,trans, trans spin label (136), or that the differences in hfscs are due to differences in geometric constraints imposed by the steroid, is difficult to assess.

EXPERIMENTAL

The ESR spectra were obtained using either a Varian V-4502 spectrometer with 100 KHz field modulation and a 9-inch magnet, equipped with a Fielddial magnetic field regulator and V-4520 temperature controller, or by a Varian E-3 spectrometer with 4-inch magnet and 100 KHz field modulation.

Quartz flat cells were used with inverted U-type mixing cells for generation of radical ions under static conditions by methods previously described (64). Electrolytic reductions were done at either a mercury or platinum cathode, the latter being especially useful when high (> 8 volt applied) potentials were used. The inert electrolyte in all cases was tetra-n-butyl ammonium perchlorate previously dried overnight under vacuum. The concentration of inert electrolyte was 0.1 N and the solutions of electrolyte-solvent were stored over molecular sieve 4A. A Heathkit Regulated L.V. Power Supply Model 1P-27 was used for the electrolysis. The flow experiment has been described by Blankespoor (21). The solutions were pumped into the flow cell using either a Buchler Multi-Staltic Pump or Compact Infusion Pump Model 975 (Harvard Apparatus Co. Inc.) rather than the gravity flow described previously.

IR spectra were recorded using either a Beckman 12A or Beckman 18A Double Beam Infrared Spectrometer. PMR spectra were obtained on a Varian A-60 NMR spectrometer or Perkin Elmer/Hitachi R-20B NMR Spectrometer. Mass spectral analysis was carried out on an Atlas CH-4 spectrometer. Gas-liquid chromatography was done on a Beckman GC 72-5 chromatograph while an Areograph Model A-90-P was used for preparative work. The polarography was done on a Northrup Electro-Chemograph Type E. Melting points were determined with a Thomas Hoover Melting Point Apparatus and are uncorrected. Microanalyses were performed by Schwarzkopf Microanalytical Laboratories.

Materials

Dimethyl sulfoxide was distilled from calcium hydride at reduced pressure and stored over molecular sieves. Potassium t-butoxide was obtained commercially and was used without further purification. If purification was needed after storage, the potassium t-butoxide was sublimed.

2,2,7,7-Tetramethyl-4,5-epoxy-octane-3,6-dione (22)

The epoxide was prepared from α-bromopinacolone by the procedure of Charpentier-Morize (36). Addition of 0.5-1.0% water was found necessary if anhydrous ether was used. The product was recrystallized from 95% ethanol:

mp 104.5-105.5° [Lit. (36) 103-105°]; pmr (CCl_4) δ 3.68 (s,2) and 1.22 (s,18).

trans-2,2,7,7-Tetramethyl-4-octene-3,6-dione (23)

Reduction of the epoxide 22 with iodide in acetic acid (36) gave a product: mp 109.6-110.1° [Lit. 109-110°]; pmr (CCl_4) δ 7.26 (s,2) and 1.20 (s,18); ir (KBr) 1669 (C=C-C=O) and 980 cm^{-1} (CH=CH).

cis-2,2,7,7-Tetramethyl-4-octene-3,6-dione (23)

Trans 23 was photolyzed as a 3% pentane solution at 2530 Å in a quartz vessel for 40 minutes (37). The product was recrystallized from 95% ethanol: mp 44-45° [Lit. 43-45°]; pmr (CCl_4) δ 6.45 (s,2) and 1.14 (s,18); ir (KBr) 1695 (C=C-C=O), 1615 (C=C), 1070, and 1010 cm^{-1} (t-BuC=O).

trans-1,4-Diphenyl-2-butene-1,4-dione

This was prepared by the method of von Pechmann (65): mp 97-98° [Lit. 96-97°]; pmr (DMSO-d_6) 7.5-8.3 (m,12); ir (KBr) 1665 (C=C-C=O), 1600 (ϕ-), and 980 cm^{-1} (C=C-H).

trans-3-Hexene-2,5-dione (34)

2,5-Dimethylfuran was brominated in methanol to give the cyclic ketal 35 according to the procedure of Levisalles (40). The ketal was not isolated but hydrolyzed with a 1% acetic acid solution to give 34. The crude product was distilled at 75-80°/10 mm [Lit. 100°/23 mm] and isolated by preparative GLC (20% Carbowax 20M at 140°): pmr (CCl_4) δ 6.69 (s,2) and 2.30 (s,6); ir (neat) 1670 (C=C-C=O) and 975 cm^{-1} (C=C-H).

cis-3-Hexene-2,5-dione (**34**)

A sample of *trans*-**34** was allowed to stand in sunlight for three weeks: pmr (CCl_4) δ 6.25 (s,2) and 2.20 (s,6); ir (neat) 1700 (C=C-C=O), 1618 (C=C, and 690 cm^{-1} (C=C-H).

5-Acetoxy-3-hexen-2-one (36)

A solution of 11.6 g (0.1 mole) 3-hexene-2,5-diol (containing 20% 3-hexyn-2,5-diol), 10.2 g (0.1 mole) acetic anhydride, and 50 ml benzene was refluxed for three hours. After removal of the solvent, the residue was oxidized. A solution of 3 g (0.03 mole) chromium trioxide in 2.9 ml sulfuric acid and 15 ml water was added to 4.7 g (0.03 moles) of the residue in 20 ml acetone. During a two hour addition, the reaction temperature was held at 0°. After stirring an additional three hours, the mixture was poured into 100 ml ether and the aqueous layer drained in a separatory funnel. After extraction twice with 50 ml water, the organic layer was washed with 50 ml saturated sodium chloride and dried over sodium sulfate. Filtration and removal of the solvent gave a residue which was distilled at 55-65°/2 mm to give 2.1 g of a mixture of 2-acetoxy-3-hexen-5-one (**36**) and 2-acetoxy-3-hexyn-5-one.

The former was isolated by GLC (20% Carbowax 20M at 170°): pmr (CCl_4) δ 6.22-6.80 (m,1), 5.21-5.70 (m,2), 2.25 (d,3), 2.05 (s,3), and 1.21-1.58 (m,3); ir (neat) 1740 (RO-C=O), 1680 (C=C-C=O), 1638 (C=C).

Tetraacetylethane

A solution of 10.8 g (0.2 mole) sodium methoxide in 50 ml methanol was added to 20 g (0.2 mole) 2,4-pentanedione and the methanol was removed on a rotary evaporator. Fifty ml ether was added to make a suspension and a solution of 25.4 g (0.2 mole) iodine in 150 ml ether was added over the period of two hours with stirring. The solid was filtered and washed with ether. The solid was placed in a separatory funnel and shaken with 100 ml water to dissolve sodium iodide present. One gram of sodium bisulfite was added to remove unreacted iodine. The material was filtered and recrystallized from acetic acid after drying to give 12.2 g (63%). This was sublimed at 110°/1 mm: mp 165-166 [Lit. 187° (66)]; pmr ($CDCl_3$) δ 16.9 (s,2) and 2.0 (s,12).

Tetraacetylethylene (40)

The dithallous salt of tetraacetylethane was treated with iodine as described by Adembri *et al*. (41). The product was recrystallized from benzene: mp 138.5-139.5° [Lit. 139-140°]; pmr ($CDCl_3$) δ 2.35 (s,12).

2,2,5,5-Tetramethyl-4-octyne-3,6-diol

A 1 ℓ 3-necked flask was fitted with addition funnel, stirrer and condenser with drying tube. Into the flask were placed 14.6 g (0.6 mole) magnesium and 300 ml ether to which 66 g (0.6 mole) ethyl bromide was added with stirring at reflux. The magnesium was allowed to react (about two hours) and the condenser outlet was fitted with a mercury bubbler to maintain about three mm head pressure. A stream of acetylene was introduced through a glass tube placed well below the solution surface. The acetylene was prewashed by passing through sulfuric acid before introduction into the flask. The rate of addition was 20-30 ml/min. The addition was continued with stirring for 30 hours. A sticky, black precipitate formed about half way through the addition but became more free-flowing during the latter stages. To the cooled acetylene Grignard reagent 60.2 g (0.7 mole) 2,2-dimethylpropanal in 50 ml ether was added dropwise maintaining the temperature at -5 to -10°. After the addition and formation of two clear layers, 250 ml saturated annomium chloride was added. The mixture was poured into a separatory funnel and 100 ml water was added to dissolve the remaining salt. The layers were separated and the aqueous layer was extracted with 100 ml ether. The organic layers were combined and extracted twice with 50 ml 5% sodium bisulfite and then with saturated sodium chloride. After drying over sodium sulfate and removal of the ether on a rotary evaporator, the solid residue was recrystallized from hexane to give 30 g (22%) of the diol: mp 113-115°; pmr ($CDCl_3$) δ 4.00 (s,2), 2.32 (s,2, $D_2O \rightarrow O$), and 1.00 (s,18); ir (KBr) 3200 (broad, OH), 1390, 1375 (t-butyl) and 1100 (C-OH); mass spectrum (70 eV) m/e (relative intensity) 198 (<1), 180 (8), 165 (10), 124 (100), 109 (30), 57 (90), and 55 (20).

Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.7%; H, 11.20%; Found: C, 72.6%; H, 10.91%.

2,2,5,5-Tetramethyl-4-octyne-3,6-dione

A mixture of 4.2 g (0.021 mole) of 2,2,5,5-tetramethyl-4-octyne-3,6-diol and 30 ml acetone was cooled to 0° and a solution of 4.2 g (0.042 mole) chromium trioxide in 15 ml water and 3.1 ml sulfuric acid was added over a period of two hours, maintaining the temperature at zero degrees. This was allowed to stir an additional 30 minutes and poured into 100 ml ether. The organic layer is separated and washed twice with 5% sodium bicarbonate, then with saturated sodium chloride. After drying over sodium sulfate and filtering, the ether was removed on a rotary evaporator. The product was recrystallized from methanol with cooling: Yield 2.7 g (65%), mp 47.5-48.5; pmr (CCl_4) δ 1.21 (s,18); ir (KBr) 1685 ($C{\equiv}C{-}C{=}O$) and 1485 cm^{-1} (t-butyl); mass spectrum (70 eV) m/e (intensity) 194 (2), 188 (2), 137 (50), 123 (50), 95 (10), 67 (14), 57 (40), 42 (100).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.2%; H, 9.36%; Found C, 74.3%; H, 9.49%.

2,2-Dipivaloylbicyclo[2.2.1]-2,5-heptadiene (42)

Four ml cyclopentadiene was placed in a flask along with 2.0 g (0.01 mole) 2,2,7,7-tetramethyl-4-octyne-3,6-dione and 10 ml chloroform was added. After standing overnight, the solvent was removed on a rotary evaporator (bath temperature 35°) and separated on a silica gel column (hexane-ethyl acetate): Yield 2.2 g (84.7%) mp ≅ 10°; pmr (CCl_4) δ 6.80 (m,2), 3.80 (m,2), 2.00-2.35 (m,2), and 1.10 (m,18); ir (neat) 1680, 1660 (C=C-C=O); mass spectrum (eV) m/e (relative intensity) 260 (1), 245 (1), 204 (80), 198 (45), 158 (10), 155 (8), 91 (10), 90 (12), and 57 (100).

Anal. Calcd for $C_{17}H_{24}O_2$: C, 78.4%; H, 9.30%; Found: C, 76.7%; H, 9.96%.

2,2-Dimethylcyclopentane-1,3-dione (50)

A 20% solution of tetramethylammonium hydroxide in methanol was added to 56 g (0.5 mole) 2-methylcyclopentane-1,3-dione (67). Approximately 240 ml were needed to reach a phenolphthalein endpoint. The solvent was removed on a rotary evaporator and the solid was dried under vacuum and pulverized. To this 250 ml methyl iodide was added and the resulting suspension was refluxed for 24 hours with stirring. The resulting mixture was placed in a separatory funnel and 200 ml ether was added. After vigorous shaking, the sodium iodide was filtered. The solvent was removed and the residue was added to 50 ml ether and shaken 5 minutes with 100 ml 5% hydrochloric acid. The aqueous layer was extracted twice with 50 ml portions of ether after neutralizing with potassium carbonate. The organic layers were combined, washed with 100 ml saturated sodium chloride and dried over magnesium sulfate. After filtration, the ether was removed on a rotary evaporator and the product was recrystallized from hexane to give 35 g (55%) of white crystals: mp 44.9-47.0° [Lit. 45-47° (65)]; pmr (CCl_4) δ 4.14 (s,4) and 1.58 (s,6), mass spectrum (16 eV) m/e (relative intensity) 126, M^+ (100) and 127, M+1 (8).

2,2-Dimethylcyclopentane-1,3-dione-Methyl ^{13}C (50)

The procedure is similar to that of the unlabeled compound above. The tetramethylammonium salt from 1.0 g 2-methylcyclopentane-1,3-dione was refluxed with 0.5 g methyl iodide (61% ^{13}C), 10 g methyl iodide, and 10 ml dioxane for 24 hours. After workup 0.34, (31%) was obtained: mp 44.5-46.5°; mass spectrum (16 eV) m/e (relative intensity) 126, M^+ (100), 127, M+1 (18).

2,2-Dimethyl-4-cyclopentene-1,3-dione (52)

This was prepared by the procedure of Agosta and

Smith (68,69): bp 60°/0.5 mm [Lit. 90°/44 mm]; pmr (CCl_4) δ 7.20 (s,2) and 1.11 (s,6).

2,2,4-Trimethyl-4-cyclopentene-1,3-dione (56) Diazomethane was added to 51 to give 2,3-diazo-7,7-dimethylbicyclo[3.3.0]octane-6,8-dione (55). This was pyrolyzed in refluxing toluene without further purification (69) to give 56. This was purified by GLC (5% SE-30 at 150°): pmr (CCl_4) δ 6.86 (q, J = 2 Hz, 1), 2.11 (d, J = 2 Hz, 3), and 1.12 (s,6).

4-Bromo-2,2-dimethyl-4-cyclopentene-1,3-dione (58) This was prepared by the method of Agosta and Smith (69): mp 79-80.5° [Lit. 75-76°]; pmr (CCl_4) δ 7.28 (s,1) and 1.21 (s,6).

2,2-Dimethylindane-1,3-dione (60) Diethyl phthalate and ethyl propionate were reacted with sodium. The resulting salt was methylated with methyl iodide to give 60 (47): mp 107-108° [Lit. 107-108°]; pmr (CCl_4) δ 5.85-5.98 (m,4) and 1.25 (s,6).

4-Methyl-1,2,4-triazolidine-3,5-dione

4-Methyl-1-ethoxycarbonyl semicarbizide was prepared from the condensation of ethyl carbazate and methyl isocyanate. This was cyclized in base by the procedure of Zinner and Deucker (70). The product was sublimed at 235°/1 mm: pmr (DMSO-d_6) δ 10.1 (s, broad, 2) and 2.85 (s,3).

4-Methyl-1,2,4-triazoline-3,5-dione (63)

A methylene chloride solution of the triazolidine dione was treated with nitrogen dioxide as reported by Stickler and Pirkle (51): mp 96-98° [Lit. 98.0-98.5°]; pmr (DMSO-d_6) δ 3.00 (s,3).

4,4-Dimethyltricyclo[5.2.1.$0^{2,6}$]-8-decene-3,5-dione (66)

The Diels-Alder reaction of 51 with cyclopentadiene gave an adduct (66) as reported (69). In addition to the endo isomer (66a) formed in 45% yield, the exo-isomer (66b) was obtained in 10% yield when the crude mixture was purified on a silica gel column (ethyl acetate-hexane): endo, mp 69-71° [Lit. 70-71°]; pmr (CCl_4) δ 5.92 (m,2), 3.41 (m,2), 1.58 (m,2), 1.00 (s,3), and 0.83 (s,3): exo, mp (64-65°); pmr (CCl_4) δ 6.22 (m,2), 3.33 (m,2), 2.70 (m,2), 1.13 (s,3), and 1.04 (s,3).

4,4-Dimethyltricyclo[5.2.1.$0^{2,6}$]decane-3,5-dione (67)

Hydrogenation of 66a over palladium-charcoal in methanol gave 67 : mp 60-61 [Lit. 60-61.5° (69)]; pmr (CCl_4) δ 3.21 (m,2), 2.69 (m,2), 1.59 (m,2), 1.1-1.5 (m,2), 1.06 (s,3), and 0.97 (s,3).

Dimethyl endo-tricyclo[3.2.2.$0^{2,4}$]-6,9-nonadiene-6,7-dicarboxylate (72a)

This was prepared by the method of Alder and Jacobs (55) in a sealed reaction tube with xylene solvent: bp

120-127°/1 mm [Lit. 95-100°/0.01 mm]; pmr ($CDCl_3$) δ 5.9-6.1 (m,2), 3.8-4.1 (m,2), 3.70 (s,6), 1.2-1.5 (m,2), and 0.45-0.70 (m,2).

Endo-tricyclo[3.2.2.$0^{2,4}$]-6,9-nonadiene-6,7-dicarboxylic acid (72b)

The diester 72a was hydrolyzed in potassium hydroxide to give the diacid (55): mp 142-143.5° [Lit. 143-144°]; ir (KBr) 3200 broad (COOH), 1700 (C=C-COOH), 1620 (C=C); mass spectrum (70 eV) m/e (relative intensity) 206 (5), 188 (11), 161 (55), 148 (22), 117 (100), 115 (85) and 46 (15).

Endo-tricyclo[3.2.2.$0^{2,4}$]-6,9-nonadiene-6,7-dicarboxylic anhydride (72c)

Fifty ml benzene was placed in a flask along with 2.1 g (0.01 mole) of the diacid and 1.2 g (0.012 mole) acetic anhydride. This was refluxed for 12 hours and the benzene and unreacted acetic anhydride were distilled under vacuum. The anhydride 72c was sublimed at 120°/0.5 mm to give 1.4 g (74%) white crystals: mp 120.9-121.5°; pmr (DMSO-d_6) 6.15-6.30 (m,2), 4.05-4.25 (m,2), 1.37-1.64) (m,2), and 0.63-1.05 (m,2); ir (KBr) 3080 (H-◁), 1840, 1780 (O=C-O-C=O), 1645 (C=C); mass spectrum (70 eV) m/e (relative intensity) 188 (27), 187 (13), 144 (25), 143 (22), 131 (11), 126 (62), 125 (100), 91 (18), 67 (26), and 66 (24).

Anal. Calcd for $C_{11}H_8O_3$: C, 70.2%; H, 4.29%; Found:
C, 70.3%; H, 4.54%.

6,7-Dichloro-endo-tricyclo$[3.2.2.0^{2,4}]$-9-nonene-endo-6,7-dicarboxylic anhydride (74)

A mixture of 9.2 g (0.1 mole) cycloheptatriene, 16.7 g (0.1 mole) dichloromaleic anhydride, and 10 ml xylene was heated in a sealed glass tube at 170° for two days. After quenching in ice water, the white crystals that formed were filtered. The product was recrystallized from acetic anhydride and sublimed at 110° 0.2 mm: mp 154-155°; pmr ($CDCl_3$) δ 5.88-6.25 (m,2), 3.50-3.72 (m,2), 1.48-1.80 (m,2), 0.44-0.80 (m,1), and 0.18-0.42 (m,1); mass spectrum (70 eV) *m/e* (relative intensity) 260 (3), 258 (5), 226 (30), 224 (100), and 196 (100).

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%.

6,7-Dichloro-endo-tricyclo$[3.2.2.0^{2,4}]$nonane-endo-6,7-dicarboxylic anhydride (75)

One gram of 74 was dissolved in 20 ml acetic acid and 0.1 g 10% palladium/charcoal was added. This was hydrogenated until the theoretical amount of hydrogen was taken up (3 hours). The product was recrystallized from ether at low temperature: mp 178-179°; pmr ($CDCl_3$) δ 2.75-2.95 (m,2), 1.10-1.70 (m,6), and 0.75-1.05 (m,2); ir (KBr) 3030 (H-◁), 1870, 1795 (O=C-O-C=O); mass spectrum (70 eV) m/e (relative intensity) 262 (2), 260 (3), 226 (33), 224 (100), 196 (25), 154 (23), 118 (42), 116 (48), 93 (51), 92 (48), and 91 (45).

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%.

Spiro[2.4]-4,6-heptadiene (77)

This was prepared by the method of Reimschneider and Schonfelder (71): bp 50°/70 mm [Lit. 52-53°/90 mm]; pmr (CCl_4) δ 6.20-6.38 (m,2), 5.80-5.97 (m,2), and 1.50 (s,4).

2,3-Dichloro-1,2,3,4-tetrahydro-1,4-(1,1-cyclopropanol-phthalic anhydride (78)

A solution of 9.2 g (0.1 mole) 77 and 16.7 g (0.1 mole) dichloromaleic anhydride in 100 ml benzene was allowed to stand one week. The benzene was removed at 30° bath temperature on a rotary evaporator. After recrystallization from acetic acid, the material was purified on a silica gel column (hexane-chloroform) to give 10.1 g (38%): mp 113.5-115.0°; pmr ($CDCl_3$) δ 6.40-6.55 (m,2), 2.80-3.01 (m,2), 0.87-1.25 (m,2), and 0.24-0.65 (m,2); ir (KBr) 1862, 1809 (O=C-O-C=O), 690 (C=C-H); mass spectrum (70 eV) m/e (relative intensity) 260 (2), 258 (3), 225 (33), 223 (100), 196 (43), 194 (14), 115 (60), 93 (95), 91 (90).

Anal. Calcd for $C_{11}H_8Cl_2O_3$: C, 51.0%; H, 3.11%, Cl, 27.4%; Found: C, 51.0%; H, 3.17%; Cl, 27.3%.

1,2-Dichloro-3,6-(1,1-cyclopano)-cyclohexane-1,2-dicarboxylic anhydride (80)

One gram of 78 was dissolved in ethyl acetate and 0.1 g palladium/charcoal was added. This was hydrogenated until one mole hydrogen was taken up (5 minutes). The solution was filtered and the solvent was removed on a rotary evaporator. The residue was recrystallized from acetic acid: mp 178.1-179.0°; pmr ($CHCl_3$) δ 1.10-2.35 (m,6) and 0.32-0.70 (m,4); ir (KBr) 1870, 1804 (O=C-O-C=O); mass spectrum (70 eV) m/e (relative intensity) 262 (.2), 260 (.3), 227 (14), 225 (40), 183 (35), 181 (11), 155 (45), 153 (15), 127 (33), 125 (100).

Anal. Calcd for $C_{11}H_{10}Cl_2O_3$: C, 50.6%; H, 3.86%; Cl, 27.2%;
Found: C, 50.5%; H, 3.74%; Cl, 27.0%.

5,6-Dichloro-7-isopropylidinebicyclo[2.2.1]-2-heptene-5,6-dicarboxylic anhydride (82)

Ten ml 7,7-dimethylfulvene and 2 g dichloromaleic anhydride were dissolved in 20 ml chloroform and allowed to stand three days. Removal of solvent on a rotary evaporator gave 2.4 g brown crystals which were purified on a silica gel column (hexane-chloroform): mp 86-89°; pmr ($CDCl_3$) δ 6.65 (m,2), 4.08 (m,2), and 1.62 (s,6).

Dimethyl 7-isopropylidinebicyclo[2.2.1]-2,5-heptadiene-2,3-dicarboxylated (84a)

This was prepared by the method of Alder and Ruhmann (72). The product was recrystallized from methanol: mp

101-102° [Lit. 101°]; pmr ($CDCl_3$) δ 7.03-7.10 (m,2), 4.37-4.45 (m,2), 3.79 (s,6), and 1.49 (s,6).

7-Isopropylidinebicyclo-2,5-heptadiene-2,3-dicarboxylic anhydride (84b)

A mixture of 1.5 g (0.06 mole) diester 84a and 25 ml 20% potassium hydroxide were refluxed under nitrogen for 12 hours. The mixture was acidified and extracted twice with 25 ml ethyl acetate. The organic layer was dried over magnesium sulfate and the solvent was removed on a rotary evaporator after filtration. The diacid was recrystallized from ethanol. This was not characterized but used to form the anhydride. One gram acetic anhydride along with 0.75 g (3.5 mmole) and 25 ml benzene were refluxed 12 hours under nitrogen and the unreacted acetic anhydride and benzene were removed by vacuum distillation. The residue was purified on a silica gel column (hexane-chloroform) giving 0.28 g (39%): mp 127-128.5°; pmr ($CDCl_3$) δ 7.08-7.13 (m,2), 3.44-3.53 (m,2), and 1.51 (s,6); ir (KBr) 1845, 1795 (O=C-O-C=O), 1618 (C=C), 682 (C=CH); mass spectrum (70 eV) m/e (relative intensity) 202 (15), 187 (35), 130 (35), 129 (50), 128 (45), 115 (100).

Anal. Calcd for $C_{12}H_{10}O_3$: C, 71.3%; H, 4.99%; Found: C, 71.3%; H, 5.00%.

Dimethyl 7-isopropylidinebicyclo[2.2.1]-2-heptene-2,3-dicarboxylate (85a)

The hydrogenation of 2.5 g (0.01 mole) of the diester 84a was done in 30 ml methanol and 0.1 g palladium/charcoal. After work up the oil was taken up in hexane and cooled until crystallization occurred: mp 56-60° [Lit. 64-65° (68)]; pmr ($CHCl_3$) 3.77 (s,6), 1.58 (s,6), and 1.20-1.90 (m,6).

7-Isopropylidinebicyclo[2.2.1]-2-heptene-2,3-dicarboxylic anhydride (85b)

A mixture of 1.5 g (0.06 mole) diester 85a and a 20% potassium hydroxide solution (25 ml) were refluxed 12 hours under nitrogen. The mixture was worked up as with 84b to give the diacid which was not characterized. Two grams acetic anhydride and 0.7 g (3.4 mmole) was refluxed 12 hours in 25 ml benzene under nitrogen. The acetic anhydride and benzene were removed by distillation under vacuum. The residue was sublimed (110°/0.2 mm) and purified by column chromatography on a silica gel column (hexane-chloroform) giving 0.53 g (79%): mp 112.5-114.0°; pmr ($CHCl_3$) δ 3.88-3.97 (m,2), 1.64 (s,6), and 1.20-2.11 (m,4); ir (KBr) 1840, 1785 (O=C-O-C=O), 1612 (C=C); mass spectrum (70 eV) m/e (relative intensity) 204 (6), 191 (5), 176 (20), 132 (100), 117 (22), 91 (10).

Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.6%; H, 5.93%; Found: C, 70.6%; H, 6.16%.

3-Methyl-3-cyclopentene-1,2-dione (**108**)

The selenium dioxide oxidation of 2-methyl-2-cyclopenteneone was carried out as described by Condon (61): mp 84-85° [Lit. 84-85°], pmr ($CDCl_3$) 7.62-7.78 (m,1), 2.95-3.10 (m,2), and 1.90-2.07 (m,2).

4-Acetoxycyclopent-2-enone (**111a**)

The procedure of DePuy *et al.* (73) was followed in the NBS bromination of cyclopenten-3-one, followed by treatment with silver acetate in acetic acid: bp 60-64°/2 mm [Lit. 57-58°/2 mm]; pmr (CCl_4) δ 7.49 (dd, J = 8 Hz, J' = 3 Hz, 1), 6.22 (dd, J = 8 Hz, J' = 2 Hz, 1), 5.65-5.85 (m,1), 2.75 (dd, J = 22 Hz, J' = 6 Hz, 1), 2.15 (dd, J = 22 Hz, J' = 3 Hz), and 2.04 (s,3).

4-Acetoxy-2-methylcyclopent-2-enone (**111b**)

2-Methylcyclopenten-3-one (61) was used in the procedure described above to give **111b**: bp 55°/0.4 mm; pmr (CCl_4) δ 7.15-7.30 (m,1), 5.55-5.80 (m,2), 2.30-3.00 (m,2), 2.03 (s,3), and 1.79 (m,3); ir (neat) 1750 (OAc), 1725 (C=C-C=O), 1645 (C=C); mass spectrum (70 eV) *m/e* (relative intensity) 154 (52), 127 (40), 112 (95), 94 (80), and 76 (100).

4-Hydroxy-2-methylcyclopent-2-enone (**112**)

One gram **111b** (0.06 mole) was refluxed for one hour in 100 ml methanol-water (50:50) with 0.1 g *p*-toluene sulfonic acid. The solvent was pulled off on a rotary evaporator and 50 ml ether was used to dissolve the residue. This was extracted with 50 ml 5% sodium bicarbonate, and washed with saturated sodium chloride. After drying over magnesium sulfate and filtration the solvent was removed by distillation. The residue was purified by column chromatography (silica gel, hexane-ethyl acetate) to give 0.3 g (41%) 112: pmr (CCl_4) δ 7.20-7.40 (m,1), 4.70-5.05 (m,1), 3.2 (s, broad, 1, $D_2O \rightarrow 0$), 2.55 (dd, J = 17 Hz, J' = 6 Hz, 1), 2.25 (dd, J = 17 Hz, J' = 3 Hz), and 1.71 (m,3); ir (neat) 3420 (-OH), 1720 (C=C-C=O), 1640 (C=C); mass spectrum (70 eV) m/e (relative intensity) 112 (60), 84 (80), 69 (80), 55 (50), 42 (100).

5-Acetoxycyclopent-2-enone (117)

A mixture of 5.7 g (0.07 mole) cyclopent-2-enone and 35 g lead tetraacetate (LTA) in 150 ml benzene was refluxed under nitrogen for three days using the method of Ellis (74). The product was decanted from the precipitate and 100 ml ether was added. The solution was washed with 5% sodium bicarbonate and saturated sodium chloride and dried over magnesium sulfate. After filtration, the solvent was removed on a rotary evaporator. The residue was purified on a silica gel column giving 2.2 g 117 (18%): [Lit. bp 72-72.5°/2 mm (75)]; pmr (CCl_4) δ 7.49 (dd, J = 5 Hz, J' = 2 Hz, 1), 6.23 (dd, J = 5 Hz, J' = 1 Hz, 1), 5.64-5.85 (m,1), 2.73 (dd, J = 17 Hz, J' = 6 Hz, 1), 2.25 (dd, J = 17 Hz, J' = 3 Hz, 1), and 2.04 (s,3).

5-Acetoxy-3-methylcyclopent-2-enone (121)

The procedure is the same as with 117. Seven grams (0.07 mole) 3-methylcyclopent-2-enone (63) gave 3.1 g (28%) 121. This was purified on a silica gel column (hexane-ethyl acetate): pmr (CCl_4) δ 5.88 (s, broad, 1), 4.99 (q, J = 7.1 Hz, J' = 3.5 Hz, 1), 2.45-3.25 (m,2), 2.14 (s,3), and 2.05 (s,3); ir (neat) 1751 (COOR), 1718 (C=O), 1620 (C=C), 1234 (C-O-C); mass spectrum (70 eV) m/e (relative intensity) 154 (1), 112 (6), 111 (5), 96 (10), 95 (3), 94 (4).

Anal. Calcd.for $C_8H_{10}O_3$: C, 62.3%; H, 6.54%; Found: C, 62.4%; H, 6.86%.

5-Acetoxy-3,4-dimethylcyclopent-2-enone (123)

The procedure is the same as with 117. 3,4-Dimethylcyclopent-2-enone (63) (3.3 g, 0.03 mole) gave 3.2 g (65%) 123. This was purified on a silica gel column (ethyl acetate-hexane). This gave a 1:2 cis/trans mixture; pmr ($CDCl_3$) trans: 5.95 (s, broad, 1), 4.78 (d, J = 3.2 Hz, 1), 2.41-3.22 (m,1), 2.16 (s,3), and 2.13 (s,3); cis: δ 5.95 (s, broad, 1), 5.25 (d, J = 7.1 Hz, 1), 2.41-3.22 (m,1), 2.16 (s,3), 2.13 (s,3), and 1.05 (d, J = 8.0 Hz, 3); ir (neat) 1750 (COOR), 1722 (C=O), 1620 (C=C), 1242

(C-O-C); mass spectrum (70 eV) m/e (relative intensity) 168 (1), 126 (12), 111 (17), 108 (16).

Anal. Calcd for $C_9H_{12}O_3$: C, 64.3%; H, 7.20%; Found: C, 64.2%; H, 7.21%.

5-Acetoxy-3,4,4-trimethylcyclopent-2-enone (125)

3,4,5-Trimethylcyclopent-2-enone (63), 5 g (0.04 mole) was reacted as with 117 to give 4.5 g (62%) 125. This was purified on a silica gel column (ethyl acetate-hexane): pmr (CCl_4) δ 5.90 (s, broad, 1), 5.10 (s,1), 2.20 (s,3), 2.10 (s,3), 1.32 (s,3), and 1.09 (s,3); ir (neat) 1750 (COOR), 1719 (C=O), 1614 (C=C) and 1235 (C-O-C); mass spectrum (70 eV) m/e (relative intensity) 182 (1), 140 (5), 125 (17), 111 (2), 109 (100).

Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.9%; H, 7.75%; Found: C, 65.6%; H, 7.96%.

4-Methylbicyclo[3.3.0]-1-octen-2-one (138)

The procedure of Conia and Leriverend (63) was used. Cyclopentyl-2-butenoate gave 138 which was purified by GLC (5% SE-30 at 150°); bp 61-64°/2 mm; pmr (CCl_4) δ 1.6-3.0 (m,9), and 1.16 (d, J = 7 cps, 3).

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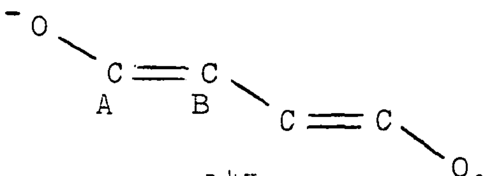
APPENDIX

Notes on Parameters Used for the McLachlan Calculation

A number of model systems were looked at to determine optimum values of h and k, which are defined:

$$\alpha_O = \alpha_C + h\beta_{CC}$$

$$\beta_{CO} = \beta_{CC} + K\beta_{CC}$$



145

To determine ρ_A/ρ_B (145) for 1,4-semidiones, the McConnell and Heller-McConnell relationships were applied to observed hfscs ($Q^H_{C-H} = 24$, $Q^H_{CCH_2} = 30$ (46)).

Table 3. ρ_A/ρ_B for 1,4-semidiones

	cyclic	ρ_A/ρ_B
cis	6-membered ring (8a)	0.08/0.25
	7-membered ring (9a)	0.08/0.21
trans	[4.4.0] (133)	0.14/0.14
	[4.3.0] (130)	0.16/0.16 (6 ring)
	acyclic	0.22/0.14 (5 ring)
trans	di-t-butyl[a] (24)	0.25/0.22

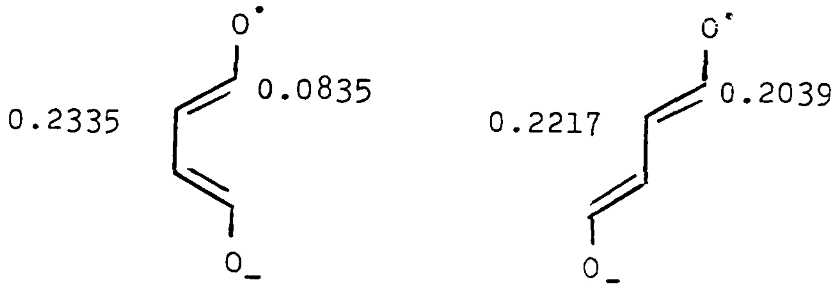
---

[a] It was assumed that $\rho_A = \rho^C_{C=O}$ for di-t-butyl-1,2-semidione because the a^H's are identical (0.2G).

A clear-cut difference exists between the cis and trans conformations about the central double bond. By proper choice of h and k the McLachlan calculation can reproduce this difference. To do this, h and k were varied and ρ_A, ρ_B calculated.

Table 4. Calculation of spin densities for a 1,4-semidione ($\alpha_C = 0$, $\beta_{CC} = 1$)

h	k	ρ_A	ρ_B
0.1	1.4	-0.0106	0.2633
0.5	1.4	0.0413	0.2438
1.0	1.4	0.1111	0.2278
1.5	1.4	0.1733	0.2155
2.0	1.4	0.2217	0.2039
2.5	1.4	0.2569	0.1927
0.4	1.4	0.0276	0.2479
0.4	1.2	0.0339	0.2052
0.4	1.6	0.0208	0.2878



145

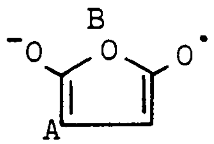
h = 0.8, k = 1.4

ρ_A/ρ_B = 0.36

h = 2.0, k = 1.4

ρ_A/ρ_B = 0.92

The 0.8 value for h was used to calculate spin densities of other radical ions of the *cis* configuration with trigonal atoms in the nodal plane.



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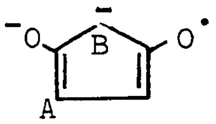

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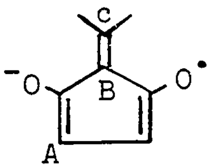
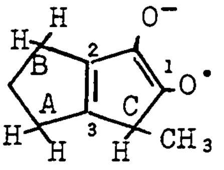


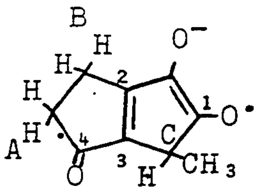
129

	20	107	129
A	0.2313	0.2326	0.2359
B	0.0350	0.0543	0.0032
C			-0.0438

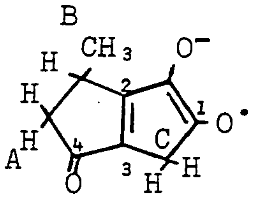
The radical produced from the oxidation of 138 was considered to have one of several likely structures 139a, 139b, or 139c.



139a



139b



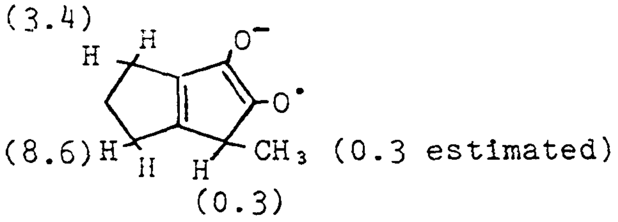
139c

The π structures of the vinyl trione radical ions 139b and 139c is the same so this reduces the M.O. calculation to two cases. The H_c splitting in each case should be small due to the opposite coefficient sign on adjacent trigonal atoms. The methyl group at position c could be several tenths of a gauss by analogy with 126, possible due to a through space interaction with spin density on the nearest oxygen.

Calculation for 139a

Position	h=1.4	1.6	1.8	2.0	2.2
	calculated spin density				
1	0.2036	0.2341	0.2615	0.2853	0.3057
2	-0.1060	-0.1117	-0.1148	-0.1157	-0.1152
3	0.3589	0.3625	0.3667	0.3707	0.3742
	calculated coefficient of ψ_4				
1	0.4087	0.4356	0.4590	0.4798	0.4981
3	-0.4589	-0.4622	0.4684	-0.4766	-0.4863

The calculated splitting constants are shown below for h=2.0.



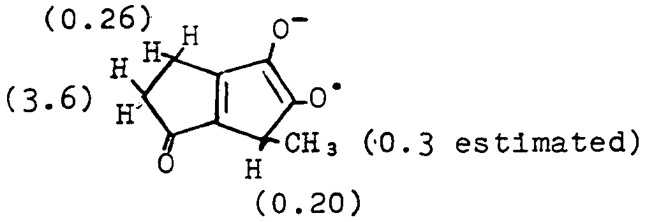
139a

(Q_{CCH_2}=30). The values a_B^H are much larger than the experimental hfsc.

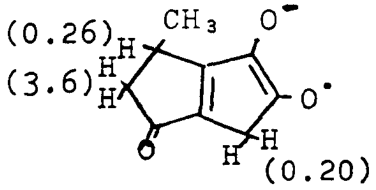
Calculation for 139b,c

Position	h=1.8	2.0	2.2	2.5
	calculated spin densities			
1	0.1314	0.1495	0.1658	0.1868
2	0.0217	0.0086	-0.0030	0.0777
3	0.2240	0.2281	0.2317	0.2362
4	0.1089	0.1183	0.1270	0.1387
	calculated coefficient of ψ_5			
1	0.3338	0.3557	0.3750	0.3995
3	-0.4192	-0.4181	-0.4190	-0.4232

Using h=2.0, the calculated hfscs for 139b and 139c are



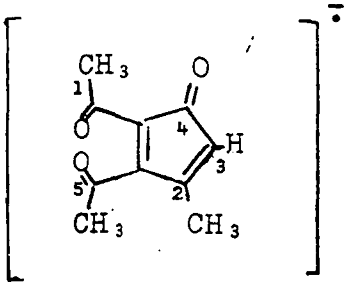
139b



139c

The 3.6G splitting is too small to account for the large (9G) triplet observed. The calculated data on the three hypothetical radicals clearly does not fit the observed hfscs.

The results of the calculation for 41 are shown below.



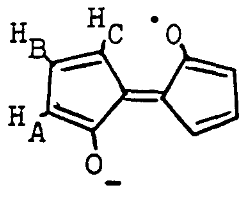
41

Assuming that h for the dione portion in the cis conformation is 0.8 (h_1,h_5) and h_4=2.5:

Calculated spin densities for 41

Position	ρ	calc. a^H (Q_{CH}=24;Q_{CH_3}=30)	a^Hobs
1	-0.0126	0.38	0.31
2	0.1329	2.62	2.04
3	0.1053	2.52	1.76
5	-0.0197	0.60	0.65

The dimers 113 and 114 were calculated using h=1.8.



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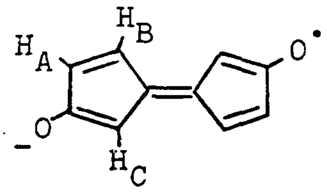

114

Calculated hfscs for **113** and **114**

Position	ρ	a^H(calc)	a^H(obs)	ρ	a^H(calc)
A	0.1492	3.58	3.2	-0.0620	1.49
B	0.0125	0.03	2.0	0.1456	3.50
C	0.1938	4.65	0.7	0.2616	6.29

The ratio of a^H(calculated) for the 1,3 dimer fit the observed hfscs fairly well although their magnitudes are about twice the observed values.