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Cyclic unsaturated semidiones and ketyls

by

Ronald Lee Blankespoor

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DOCTOR OF PHILOSOPHY

Major Subject: Organic Chemistry

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Signature was redacted for privacy.
In Charge of Major Work

Signature was redacted for privacy.
For the Major Department

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For the Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1971

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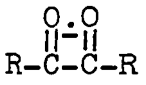
INTRODUCTION

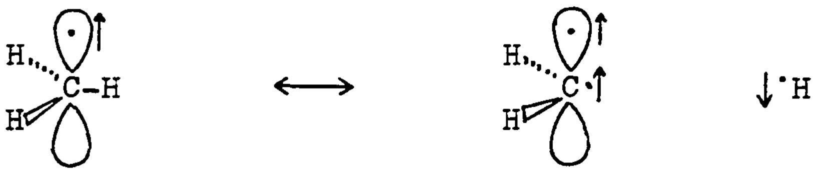
In 1964 Russell and Strom (1) reported that the one electron reduction product of a diketone, the semidione, 1, serves as an excellent spin label for the introduction of an unpaired electron into aliphatic systems. Numerous publications have since resulted on studies of semidiones in saturated ring systems (1-13). The interpretation of the electron spin resonance (ESR) spectra obtained from these paramagnetic molecules has been used in an analytical manner in studies of structural and conformational problems (1-8, 12, 14, 15).



$$\overset{O\;\cdot\;O}{\overset{\|\;-\;\|}{R-C-C-R}}$$

1

The interpretation of ESR spectra has also been used as a means of studying various types of interactions between the unpaired electron and nuclei in the molecule possessing a non-zero net magnetic moment. One such interaction is that between an electron in a p-orbital of an sp^2 carbon with a hydrogen attached as for example is found in methyl radical, 2. Although the hydrogen lies in the nodal plane of the molecule, hyperfine splitting of the hydrogen is observed as a result of spin polarization which places a spin density on



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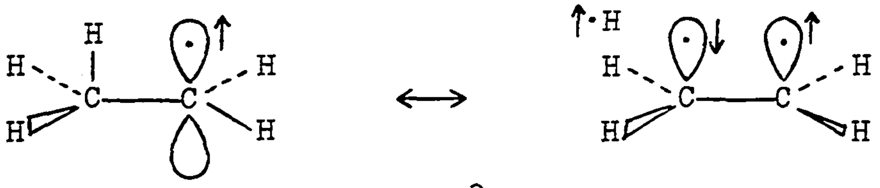
the hydrogen which is opposite to that seen by the molecule as a whole. The magnitude of this interaction is given by McConnell's equation (16), $a^H = -24\rho_C$, where ρ_C is the spin density in the p_z orbital of the carbon atom. Since spin densities can also be calculated by the modified Hückel Molecular Orbital (MO) treatment of McLachlan (17), comparisons can be made between calculated and observed spin densities.

A second interaction between hydrogen atoms and an unpaired electron that is commonly encountered occurs for the β-hydrogens of ethyl radical, 3, where the hydrogen atoms are attached to a carbon atom adjacent to the unpaired spin. This interaction is commonly described as hyperconjugation and is maximum when the carbon-hydrogen bond and orbital are coplanar (18). The hyperconjugation interaction follows a $\cos^2\theta$ relation, $a^H = \beta\rho_C\cos^2\theta$, where θ is the dihedral angle between the C-H bond and the p orbital and β is a constant of approximately 40 (19). Since the $\cos^2\theta$ value for a freely rotating methyl group is 0.5, the absolute value of the hyperfine splitting constant (hfsc) for the β-hydrogens in ethyl radical should be similar in magnitude to the α-hydrogens which



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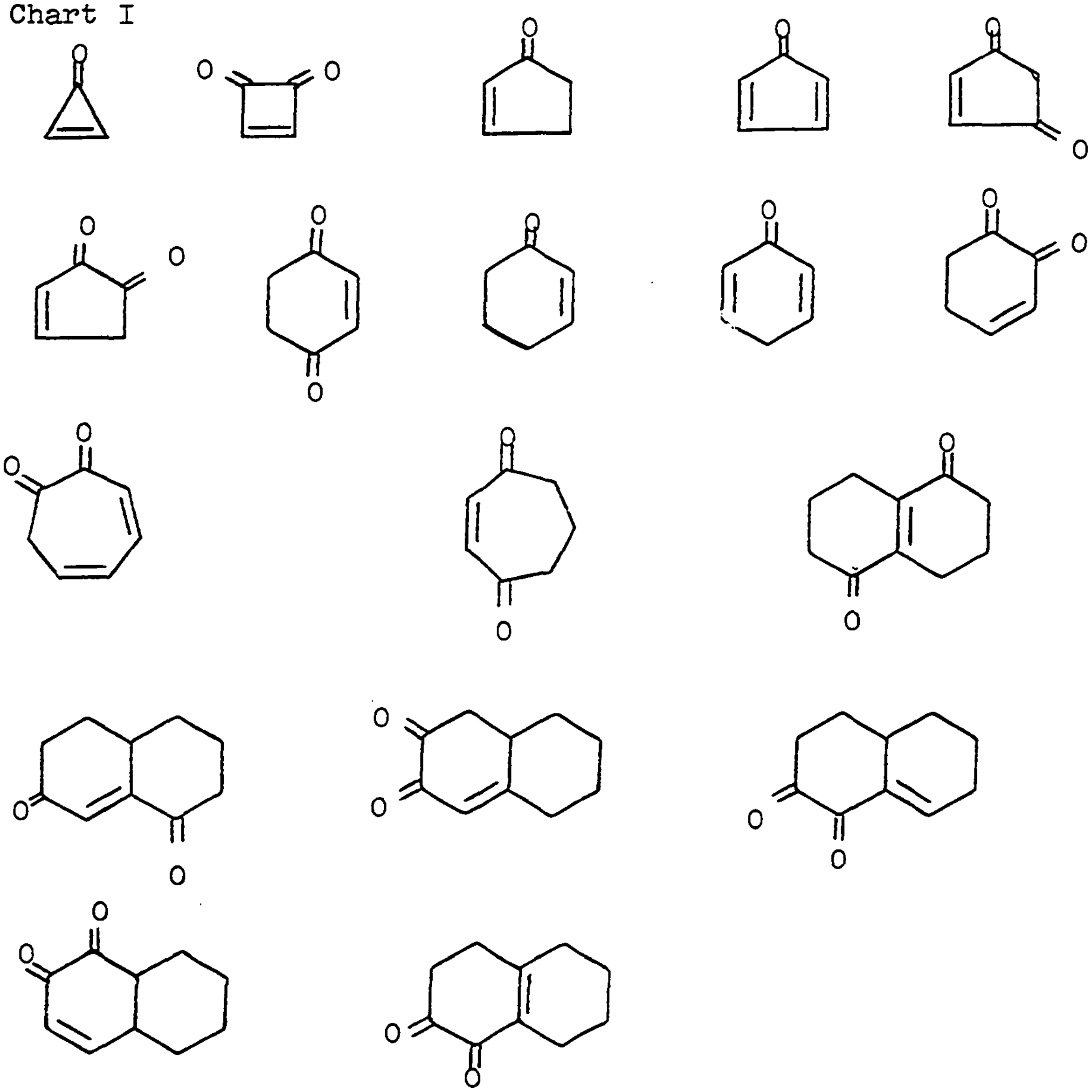
interact with the unpaired electron by spin polarization. This is in fact observed since the hfsc's for the α and β hydrogens of ethyl radical are 22.4 and 26.9 G, respectively.

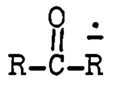
This work was undertaken to extend ESR studies to cyclic systems which contain sites of unsaturation such as double bonds (Chart I) and to utilize these ESR studies as a probe

Chart I



for investigating conformational and structural problems. The large number of naturally occurring compounds with polycyclic structures containing double bonds provided impetus for these studies. It was necessary, however, to initially acquire a complete understanding of the monocyclic systems as models before proceeding to the more complex systems. The semidione was chosen as the spin label since it is readily formed and is generally quite stable (1).

The presence of one or more double bonds in conjugation to an unpaired electron in a spin label is also of interest since spin densities can be determined for the sp^2 hybridized carbons with the use of McConnell's equation and comparisons can be made to spin densities calculated by Hückel MO theory. In this aspect of the work, the ketyl, 4, which is the one electron reduction product of a ketone, was used as a spin label in addition to the semidione as a means of generating the paramagnetic molecules.



$R-\overset{\overset{O}{\|}}{C}-R^{\dot{-}}$

4

Semidiones and ketyls can be generated by reduction of a diketone and ketone, respectively, either electrolytically, with alkali metal, or by electron transfer from basic solutions of dimethyl sulfoxide (DMSO). The best yields of semidiones are obtained by treating equimolar amounts of a hydroxy ketone and a diketone with basic solutions of DMSO.

$$RCOCH(OH)R + B^{-} \rightleftarrows RC(O^{-})=C(O^{-})R$$

$$RC(O^{-})=C(O^{-})R + RCOCOR \rightleftarrows 2\ RC(O^{\cdot})=C(O^{-})R$$

Dissolution of unsaturated hydroxy ketones and unsaturated ketones in basic DMSO under static conditions frequently resulted in the formation of unstable radicals which decayed before detection was possible. It was necessary, therefore, to react the two components in a flow system (see Figure 1) in which the time interval between mixing and detection was about 0.1 sec at maximum flow. By stopping the flow, the lifetime of the radical under observation could be determined by monitoring its rate of decay. Radicals with lifetimes of only several seconds could be detected with this flow system.

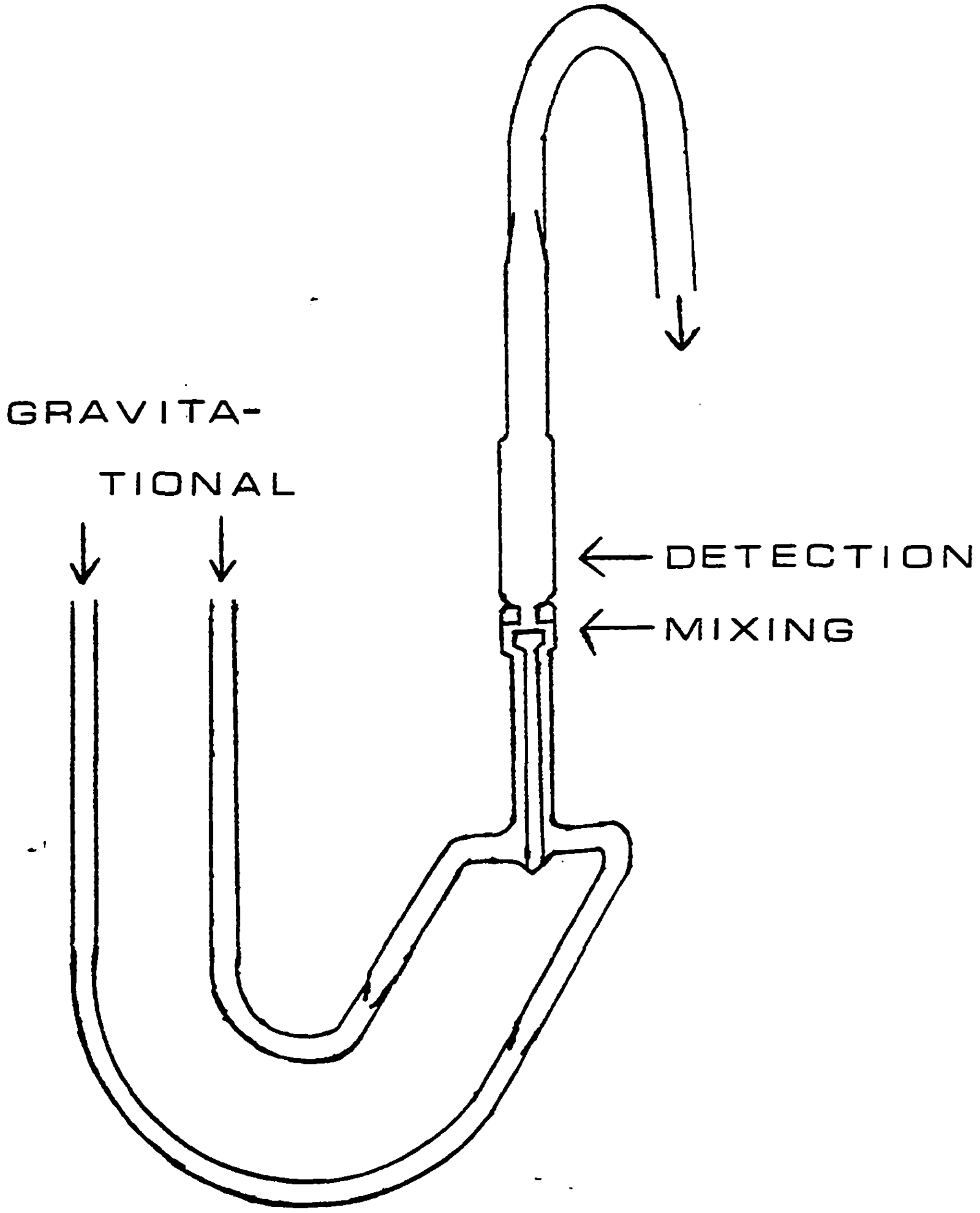


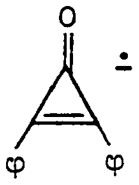
Figure 1. Flow system used for detecting transient radicals in DMSO solutions

CYCLIC UNSATURATED KETYLS

Although ketyls of saturated compounds such as hexamethyl acetone are known (20), the presence of α-hydrogens greatly reduces the stability of the radical anion. Recently, however, the short-lived ketyl of acetone has been observed at room temperature by the radiolysis of basic, aqueous solutions of isopropyl alcohol in a flow system (21).

The reduction of benzophenone to form the radical anion ketyl has been known for about 80 years (22). More recently, both electrolytic reduction of benzaldehyde (23) and photolysis of basic solutions of benzaldehyde (24) have resulted in the formation of the ketyl which has been observed with ESR spectroscopy.

Attempts to reduce diphenylcyclopropenone to the ketyl 5 with Na/K alloy (25) resulted in the formation of a radical whose ESR spectrum was consistent with biphenyl radical anion, 6, which had previously been seen by Carrington and co-workers (26). Reaction of diphenylcyclopropenone in DMSO (0.04 M)



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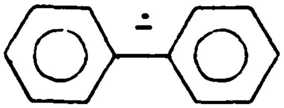

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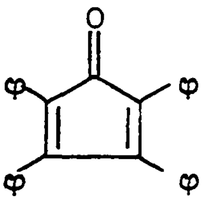
with a solution of potassium t-butoxide in DMSO (0.08 M) under flow conditions with a time interval between detection and mixing of 0.5-1.0 sec gave a radical with a lifetime of 30-60 seconds. The large number of lines in the ESR spectrum (Figure 2) rules out both 5 and 6 as possible structures for the radical under observation.

Recently, it was reported that the reduction of diphenylcyclopropenone with Mg-MgI_2 (27) and Al-Hg (28) gave small amounts of both 7 and 8. The radical anion of 7 has been observed by Ray and co-workers (29) and can be eliminated as the possible radical in Figure 2 by comparison of spectra. The structure 8 cannot be eliminated without generation of its radical anion.



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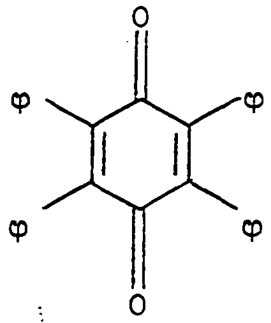

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Both 9 and 10 are possible unsaturated ketyls in the four-membered ring. Reduction of the zwitterion, 11,

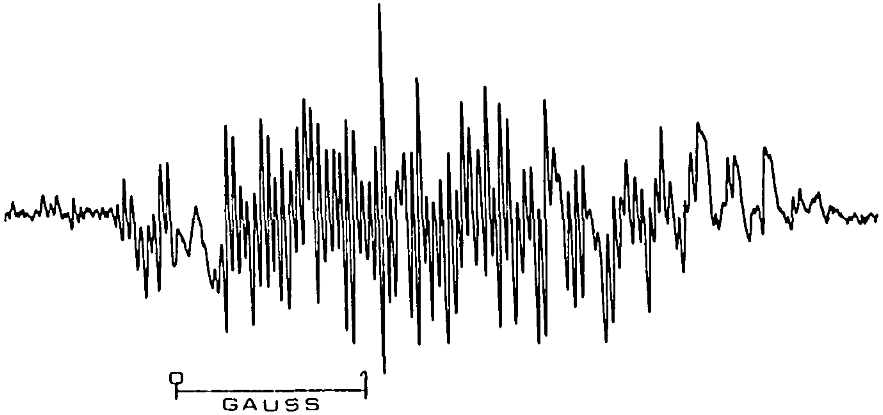
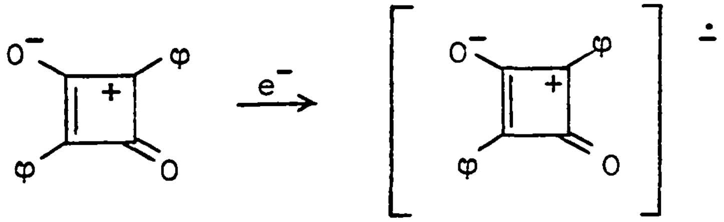
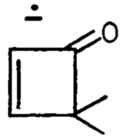


Figure 2. The first derivative ESR spectrum of the radical obtained from the reaction of diphenylcyclopropenone with basic DMSO under flow conditions at 25°



11 9



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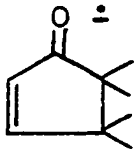
failed to give rise to 9 as observed by ESR spectroscopy. No attempts have been made to generate 10. Both possible unsaturated ketyls in the five-membered ring, 12 and 13, have been observed.



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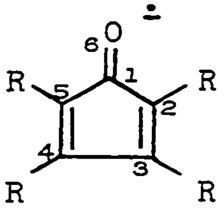


13

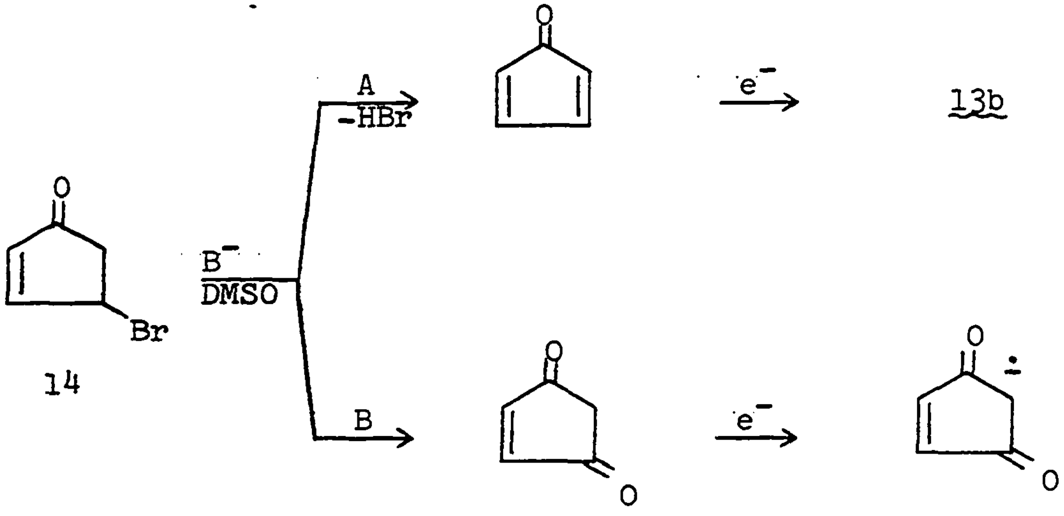
a, R = Ph
b, R = H

Attempts to reduce 2-cyclopentenone, 5,5-dimethyl-2-cyclopentenone, and 4,4-dimethyl-2-cyclopentenone electrolytically in DMF at -60 or +25 (30) gave no ESR signal. However, reduction of 4,4,5,5-tetramethylcyclopentenone where both the enolic and allylic protons have been substituted with methyl groups did give an ESR signal of 12 (30). The analysis of the spectrum gave hyperfine splitting constants of a^H = 0.45 (1H), 11.0 (1H), and 0.64 (6H) G. The assignments of the small doublet coupling to the 2-position and the 0.64 coupling for six hydrogens to the two equivalent methyl groups at the 4-position were made on the basis of Hückel and McLachlan MO calculations. Russell and Stevenson also observed that the substitution of the double bond in 2-cyclopentenone with a benzo group resulted in stabilization of the ketyl since they were able to observe the unsubstituted ketyl of 1-indanone at room temperature.

Ray and co-workers (29) reported that tetraphenylcyclopentadienone could be reduced with alkali metal in THF to give 13a. In THF 13a had hyperfine splitting constants of a^H = 0.14 (4H), 0.28 (4H), and 0.56 (12H) G. On the basis of these coupling constants it was suggested that the phenyl groups were twisted 30° from the plane of the five-membered ring.

The precursor to 13b, cyclopentadienone, is a non-isolable compound and has only been postulated as a reaction intermediate (31). It was necessary, therefore, to generate cyclopentadienone under conditions where it could readily be reduced to 13b. Moreover, 13b itself has only a short lifetime and special conditions were required for its detection. These conditions are met in a DMSO flow system.

When 4-bromo-2-cyclopentenone, 14, was reacted with potassium t-butoxide in DMSO under flow conditions, a radical with a lifetime of about 3-5 seconds was recorded. The ESR spectrum of this radical shown in Figure 3 is a triplet of triplets with a^H = 2.91 (2H) and 5.27 (2H) G. Under these conditions it was necessary to consider both 13b and 15 as possible structures for this radical arising from paths A and B, respectively.

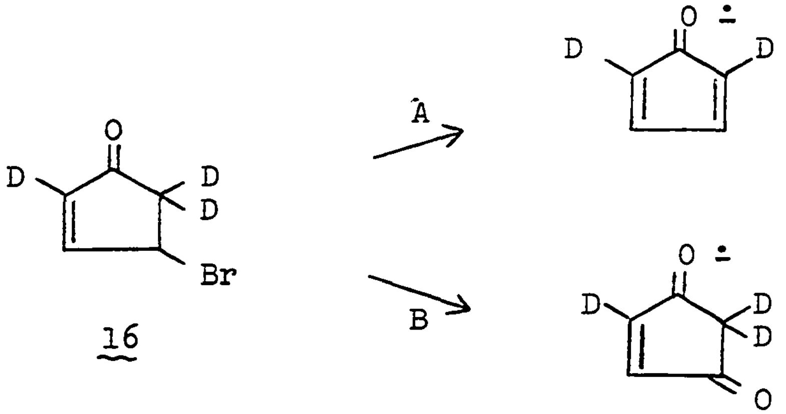


15

In path A the bromo ketone reacts with the strong base to eliminate a molecule of HBr generating cyclopentadienone. The cyclopentadienone is then reduced by electron transfer from the basic DMSO to give the ketyl 13b. In path B the bromo ketone reacts with the basic DMSO to form the intermediate diketone which is reduced by solvent to the unsaturated 1,4-semidione, 15.

Figure 3. The first derivative ESR spectrum of cyclopentadienone ketyl, **13b**, in DMSO at 25°

This problem was experimentally resolved by the synthesis of the trideuterio-substituted bromo ketone, 16. In the absence of proton exchange with DMSO 16 reacts with



16

17

18

basic DMSO by paths A and B to form 17 and 18, respectively. The ESR spectrum recorded from the reaction of 16 with basic DMSO under flow conditions is shown in Figure 4 and has hyperfine splitting constants of a^H = 5.27 (2H) and a^D = 0.46 (2D) G. This clearly eliminated 18 as the structure of the radical and is consistent with the cyclopentadienone ketyl (17). The deuterium coupling of 0.46 G is also consistent with the substitution of a 2.91 G hydrogen splitting in 13b. The calculated and observed spin densities for 13b and their assignments are given in Table 1. Good agreement is obtained both in assignment and in magnitude of the spin densities.

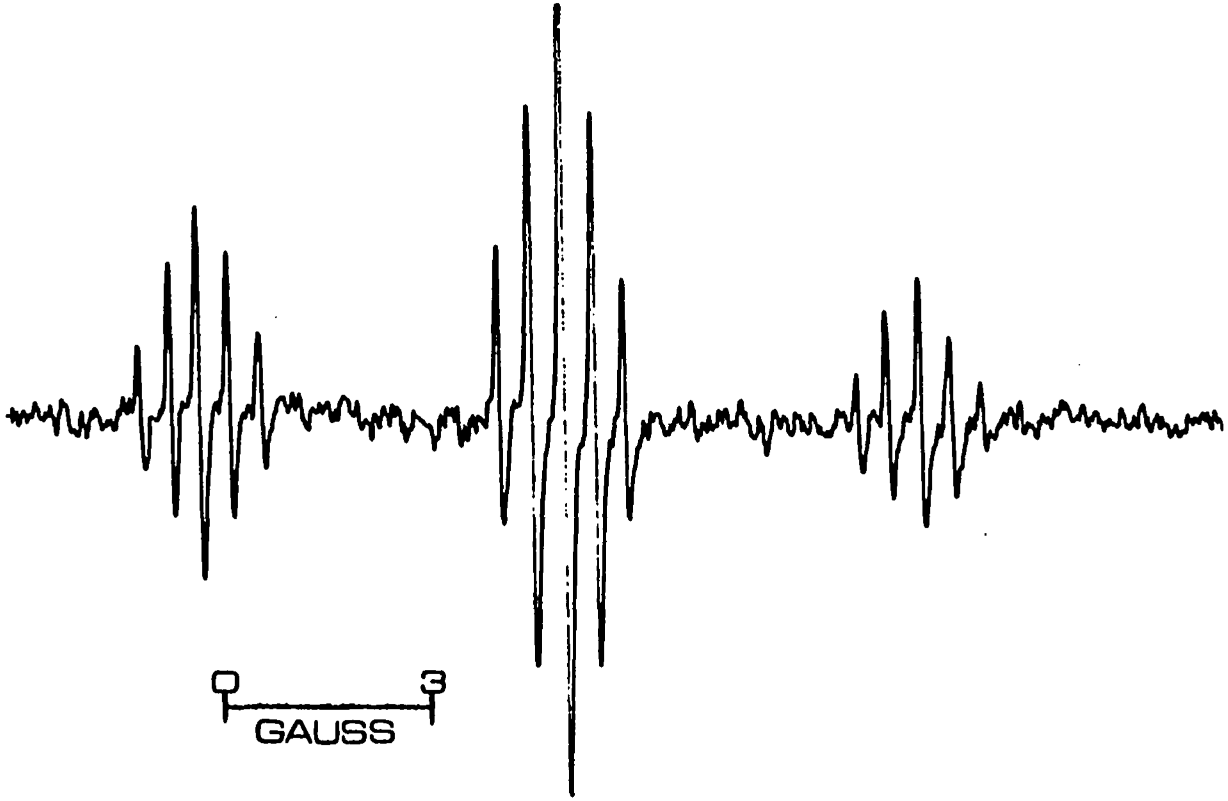


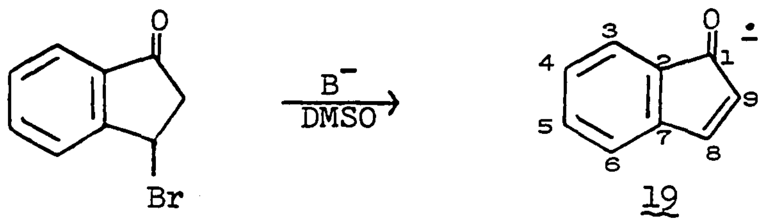
Figure 4. The first derivative ESR spectrum of 2,5-dideuteriocyclopentadienone ketyl, 17, in DMSO

Table 1. Observed and calculated spin densities of 13b[a]

Position	Calculated Hückel	Calculated McLachlan	Observed
1	0.2355	0.2515	
2,5	0.1164	0.0905	0.1220
3,4	0.1770	0.2022	0.2220
6	0.1779	0.1630	

[a] $\beta_{C=O} = 1.4\beta_{CC}$; $\alpha_O = \alpha_C + 1.8\,\beta_{CC}$.

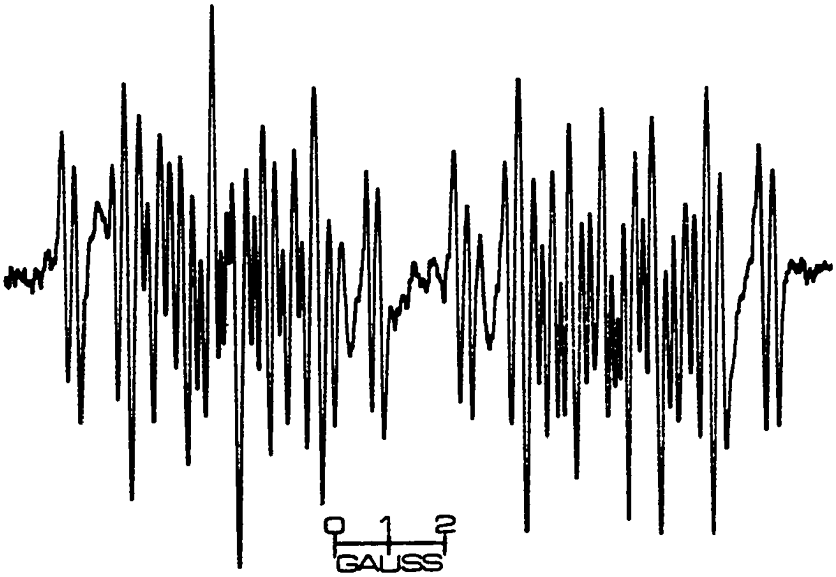
Reaction of 3-bromo-1-indanone with potassium t-butoxide in DMSO under flow conditions gave rise to the formation of the indenone ketyl, 19. The ESR spectrum of 19 is shown in Figure 5 and gives hfsc of a^H = 7.10 (1H), 1.94 (1H),



19

1.50 (1H), 1.15 (1H), 0.91 (1H), and 0.20 (1H) G which have been assigned in Table 2 based on the calculated Hückel and McLachlan spin densities. Electrolytic reduction of indenone gave a polymer without an ESR signal (30). Although 19 is more stable than cyclopentadienone ketyl, 13b, its lifetime at room temperature in DMSO was only several minutes.

Figure 5. The first derivative ESR spectrum of indenone ketyl, 19, (top) in DMSO; calculated spectrum (bottom) for Lorentzian linewidth 0.13 gauss and splitting constants from text performed by HEOLCO JNM-RA-1 spectrum accumulator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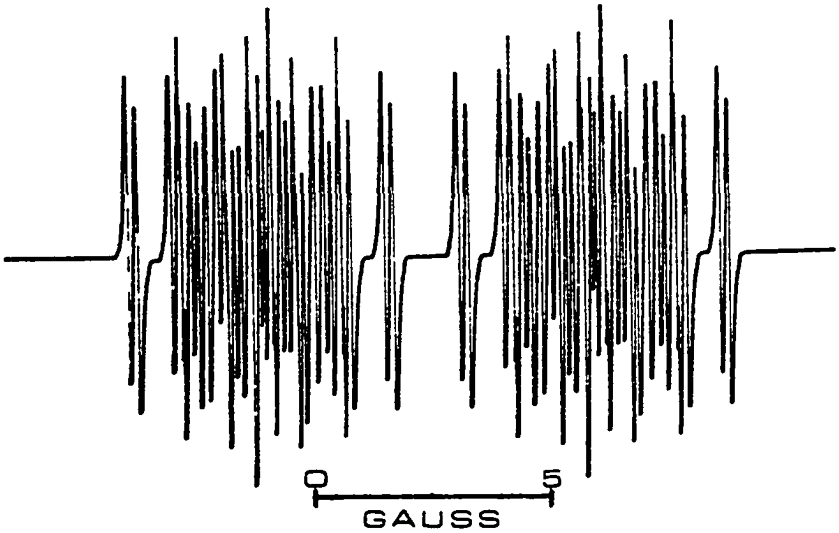
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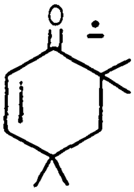
Table 2. Observed hyperfine splitting constants (G) and calculated spin densities of 19[a]

Position	a^H	Calculated spin densities	
		Hückel	McLachlan
C-1		0.2248	0.2601
C-2		0.0609	0.0696
C-3	0.91	0.0551	0.0313
C-4	1.94	0.0586	0.0599
C-5	1.50	0.0574	0.0463
C-6	1.15	0.0563	0.0445
C-7		0.0597	0.0555
C-8	7.10	0.2296	0.3209
C-9	0.20	0.0645	0.0090
O-		0.1330	0.1210

[a] $\beta_{C=O} = 1.4\ \beta_{CC}$; $\alpha_O = \alpha_C + 1.8\ \beta_{CC}$.

Electrolytic reduction of 4,4,6,6-tetramethylcyclohexenone, 4,4-dimethylcyclohexadienone, and 6,6-dimethylcyclohexadienone gave rise to the radical anion ketyls, 20, 21 and 22, respectively (30).



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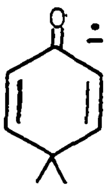

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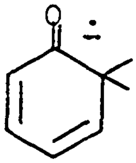

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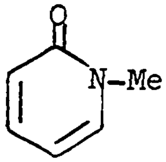

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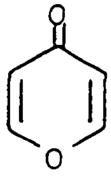

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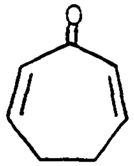

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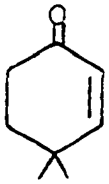

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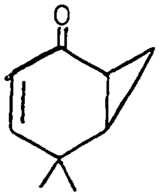

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The assignments of hyperfine splitting constants (hfsc) for 20 - 22 are given in Table 3. Excellent agreement was obtained by comparison to Hückel and McLachlan MO calculations (30). An attempt to reduce 4,4,6,6-tetramethylcyclohexenone and 23 - 27 to their corresponding ketyls with basic DMSO under flow conditions failed.

Table 3. Observed hfsc (G) of 20, 21 and 22

Position	20	21	22
C-1			
C-2	0.80	1.14	1.33
C-3	11.80	7.05	8.08
C-4	0.80[a]		1.33

---

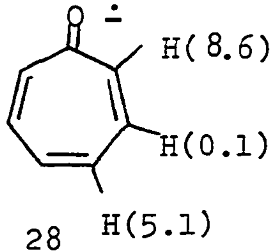
[a] $a_{CH_3}^{H}$.

Table 3 (Continued)

Position	20	21	22
C-5	0.34	7.05	9.40
C-6		1.14	0.08[a]

Treatment of 4,4-dimethylcyclohexadienone with potassium t-butoxide in DMSO under flow conditions did give rise to 21. The ESR spectrum recorded for 21 under these conditions is shown in Figure 6 and has hyperfine splitting constants of a^H = 1.19 (2H) and 7.13 G (2H) G. No attempts has been made to reduce 6,6-dimethylcyclohexadienone with basic DMSO solution under flow conditions.

In 1968 Ikegami and Seto reported (32) that tropone could be reduced at low temperatures to form the ketyl 28. Interestingly, the assignment of the small coupling constant



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to the position β to the carbonyl is in accord with McLachlan calculations which gives spin density values for the α, β, and γ carbon atoms of 0.3722, -0.0202, 0.1843, respectively. 2,7-Dimethyltropone ketyl gave a spectrum consistent with 28 with $a_\beta^H = 0.48$, $a_\gamma^H = 4.77$, and $a_{CH_3}^H = 8.76$ H (2). Reduction of tropone with potassium t-butoxide in DMSO under flow

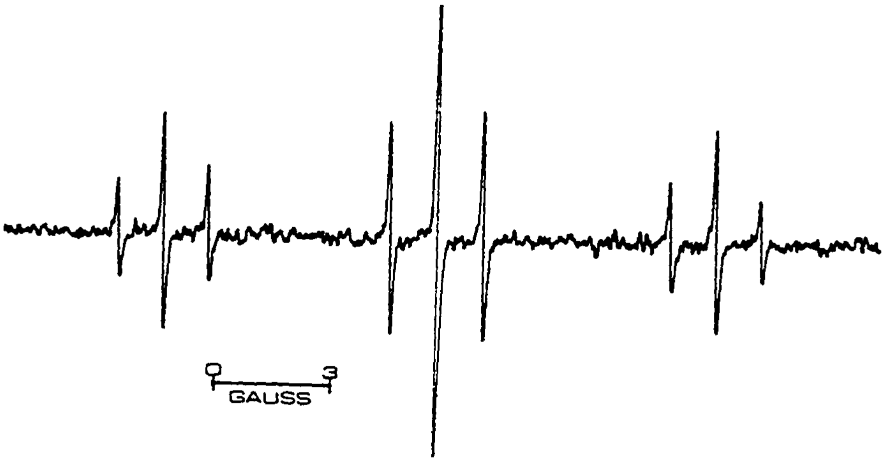


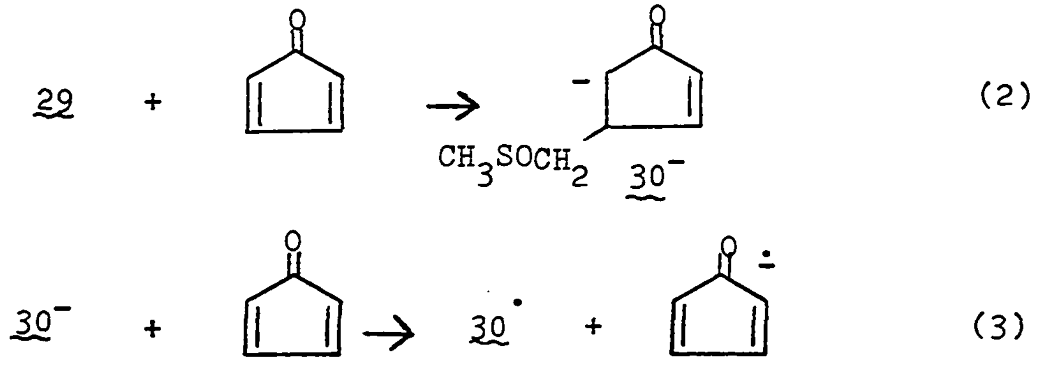
Figure 6. The first derivative ESR spectrum of 4,4-dimethylcyclohexadienone ketyl, 21, in DMSO

conditions at room temperature also gave the tropone ketyl. The ESR spectrum of tropone ketyl in DMSO is shown in Figure 7 and is consistent with a^H = 8.59 (2H), 0.12 (2H), and 5.03 (2H) G. Russell and Stevenson (30) were unable to observe 28 by the room temperature electrolytic reduction of tropone.

The ability of solutions of potassium t-butoxide in DMSO to reduce dienones and tropone is surprising. In addition to 4,4,6,6-tetramethylcyclohexenone and 23 - 27, attempted reductions under similar conditions of di-t-butyl ketone, benzophenone, and di-isopropyl ketone failed even though benzophenone is readily reduced by a variety of agents. The reduction of the dienones and tropone possibly involves the formation of the methylsulfinylcarbanion, 29, as is illustrated in Scheme I for the formation of cyclopentadienone

Scheme I

$$CH_3SOCH_3 + t\text{-}BuO^- \rightleftarrows t\text{-}BuOH + \underset{29}{CH_3SOCH_2^-} \qquad (1)$$



$30^{\bullet} \rightarrow$ non-radical products (4)

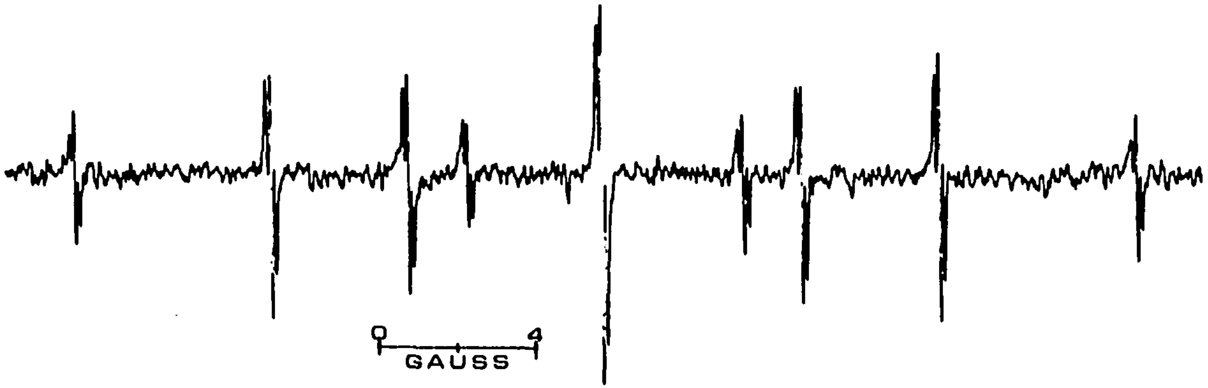
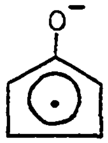


Figure 7. The first derivative ESR spectrum of tropone ketyl, 28, in DMSO

ketyl. The electron transfer from the enolate, 30$^-$, to the dienone in Step 3 is not unexpected since Russell and co-workers (33) have observed electron transfer from enolates to nitro aromatics. Saturated ketones are not reduced by their enolate anions. The inability of basic DMSO to reduce benzophenone apparently reflects the absence of an enolate ion in this solution.

Interestingly, the assignments of spin densities in the various unsaturated ketyls are also predicted by the simple Hückel and McLachlan MO calculations. This agreement also exists for the tropone ketyl which is the only ketyl studied that has a low spin density at the position β to the carbonyl.

The hfsc's for tropone ketyl are significantly larger than those observed for the cyclopentadienone ketyl. This can be explained by an examination of resonance structures 31 - 34 on the basis of the Hückel Rule where a ring system containing 4n π-electrons is non-aromatic and a ring system containing 4n + 2 π-electrons is aromatic (n = 1,2,···). In contrast to 31 which has 5 π-electrons in the ring, 32 has 6 π-electrons in the ring and is therefore aromatic. The



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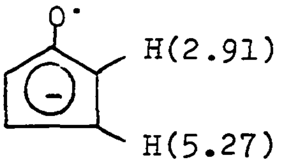

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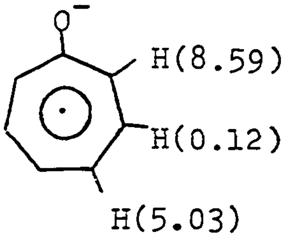

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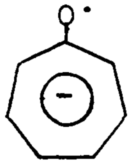
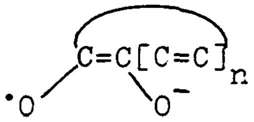


34

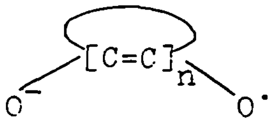
enhanced resonance contribution of 32 over 31 results in low spin density in the ring and consequently small coupling constants which is observed. Resonance structure, 33, has 7 π-electrons in the ring as compared to 8 π-electrons in 34. Therefore, 34 being less aromatic should have a decreased resonance contribution. This results in a high spin density in the ring of tropone ketyl and consequently large coupling constants. The McLachlan MO calculations are also consistent with these observations where a total spin density of 0.4145 resides in the carbonyl of cyclopentadienone ketyl and -0.0722 resides in the carbonyl of tropone ketyl.

CYCLIC UNSATURATED SEMIDIONES

Two types of unsaturated conjugated semidiones are possible in ring systems. In 35 (n = 1, 2, 3, etc.) the double



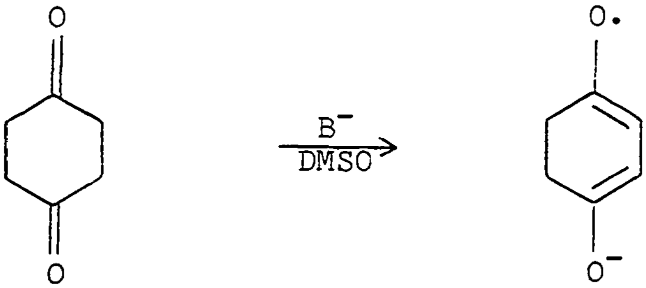
35



36

bond(s) are conjugated externally to a 1,2-semidione whereas in 36 (n = 2, 3, etc.) the double bonds are conjugated internally to give 1,4; 1,6; etc. semidiones.

The only reported examples of unsaturated semidiones in monocyclic systems are 1,4-semidiones. Russell and co-workers (7) have prepared cyclohexene-1,4-semidione, 37, by the treatment of cyclohexane-1,4-dione with potassium t-butoxide

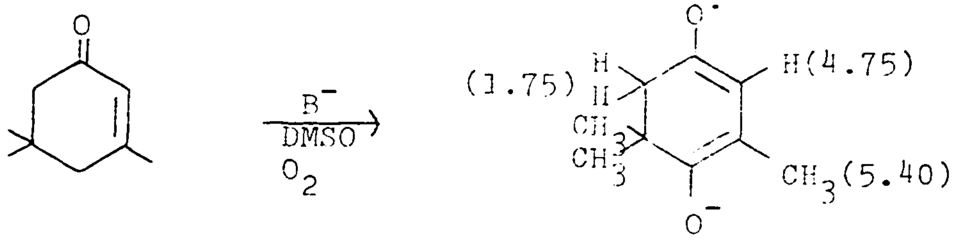


37 a^H = 5.79 (2H),
2.35 (4H) G

in DMSO solution. In the absence of oxygen, 37 can be observed for several hours in basic DMSO solution (7).

Exposure of 37 in basic DMSO to oxygen results in the formation of p-semiquinone.

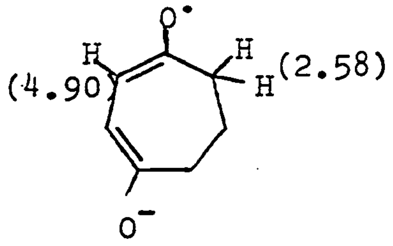
The methyl-substituted cyclohexene-1,4-semidione, 38, was prepared (34) by the oxidation of the α,β -unsaturated ketone in basic DMSO.



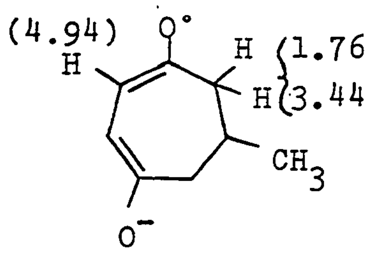
38

The methyl hfsc of 5.40 G is similar in magnitude to the hfsc for the hydrogen in 37 (5.79 G) which it replaces. The methyl hydrogens and hydrogen interact with the unpaired electron in the p-orbital of the carbon atom to which they are attached by hyperconjugation and spin polarization, respectively, in direct analogy to the previously discussed ethyl radical. This results, therefore, in the observed similarity in magnitude of hfsc's.

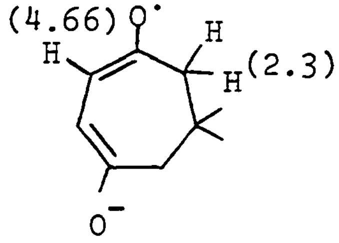
Several examples of unsaturated semidiones in the seven-membered ring are also known. The 1,4-semidiones, 39,[1] 40, and 41 (35) have been prepared by electrolytic reduction of their corresponding endiones.



39

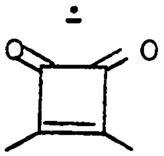


40

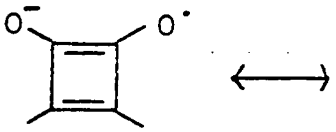


41

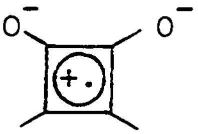
The only unsaturated semidione in the four-membered ring, 42, can be considered as both a 1,2- and 1,4-semidione.



42



43



44

This radical would be of considerable interest since resonance structures such as 43 would be unfavorable based on the Hückel Rule. On the same basis 44 as a 3 π-electron system might be a better resonance contributor resulting in the observation of high spin density in the ring. About 100 mgs

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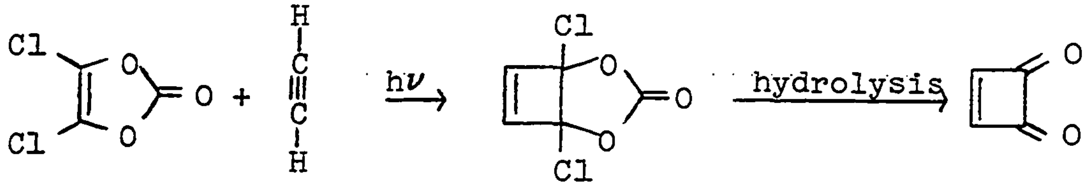
[1] J. Dodd, Postdoctoral Fellow with G. Russell, Iowa State University, Ames, Iowa. Private communication, 1970.

of dimethylcyclobutenedione were received as a gift from Dr. Chickos. However, attempts to reduce this diketone with basic DMSO under static conditions or electrolytically from -70 to +25 to form 42 were unsuccessful.

Recently, Hinshaw has reported (36) the first successful synthesis of cyclobutenedione outlined in Scheme II.

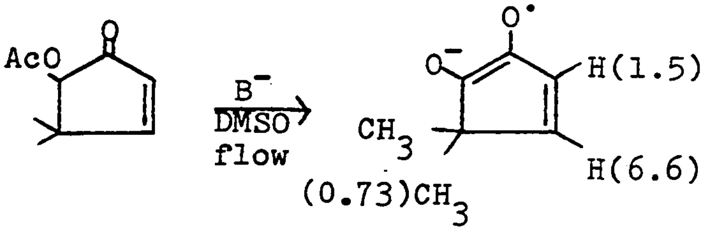
Scheme II



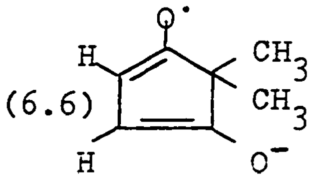
45

Several grams of the cycloadduct, 45 are presently being prepared with the intention of reacting this material with basic DMSO under flow conditions to generate cyclobutenedione and reducing it under these conditions to the semidione. In view of the results on dimethylcyclobutenedione, success is not likely.

Preparation of both the unsaturated 1,2-semidione 46 and the 1,4-semidione 47 in the five-membered ring has been



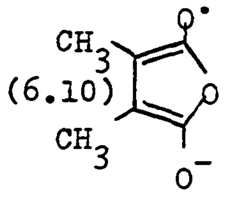
46



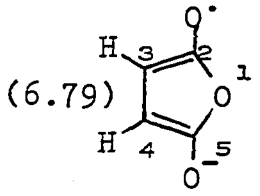
47

achieved.[2] Since 5,5-dimethylcyclopent-3-en-1,2-dione is unknown, 46 was generated by reacting the acetoxy ketone with potassium t-butoxide in DMSO under flow conditions. Reduction of 5,5-dimethylcyclopent-2-en-1,4-dione either electrolytically or with basic DMSO under flow conditions gave rise to the formation of 47. Both radicals were very unstable in DMSO at room temperature and had lifetimes of 5-10 seconds. The lack of significant hyperfine splitting in the methyl hydrogens of 47 is rather surprising. This observation could possibly result from the fact that the methyl groups are lying in the nodal plane of the highest occupied molecular orbital.

Nelsen and Seppanen (37) have observed the formation of the one electron reduction product of dimethylmaleic anhydride, 48a, by electrolysis. In addition, the radical anion of maleic anhydride, 48b, has recently been observed in these laboratories[3] by the reduction of maleic anhydride



48a



48b

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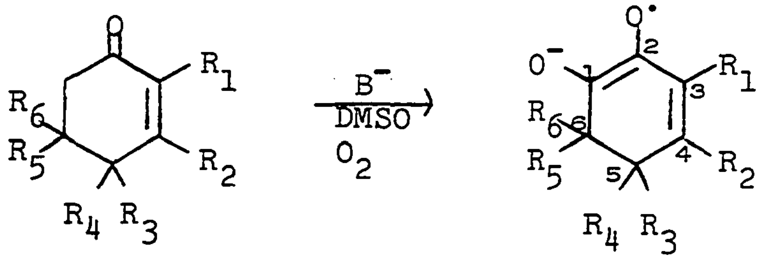
[2] J. Mattox and R. Penny, Iowa State University, Ames, Iowa. Private communication, 1971.

[3] R. B. Brainard, Postdoctoral with G. Russell, Iowa State University, Ames, Iowa. Private communication, 1971.

in basic DMSO under flow conditions. Interestingly, the 6.1 gauss coupling for the methyl groups in 48a and the 6.79 gauss coupling for the hydrogens in 48b indicate that there is comparable spin density at the C-3 and C-4 positions in 48 to the analogous carbon atoms in 47 where the hydrogen atoms have a 6.6 gauss coupling.

An attempt to generate the conjugated unsaturated 1,2-semidiones, 49, in the six-membered ring by the treatment of a variety of methyl-substituted α,β-unsaturated cyclohexenones, 50, with basic DMSO and oxygen was unsuccessful. A second attempt that was successful utilized a recent report by Ellis (38) where he found that the reaction of 50a with lead tetraacetate in benzene under reflux for 2-3 days gave a 78%



50 49

a, $R_1=R_3=R_4=H$
$R_2=R_5=R_6=CH_3$

b, $R_1=R_3=R_4=R_5=H$
$R_2=R_6=CH_3$

c, $R_2=R_5=R_6=H$
$R_1=R_3=R_4=CH_3$

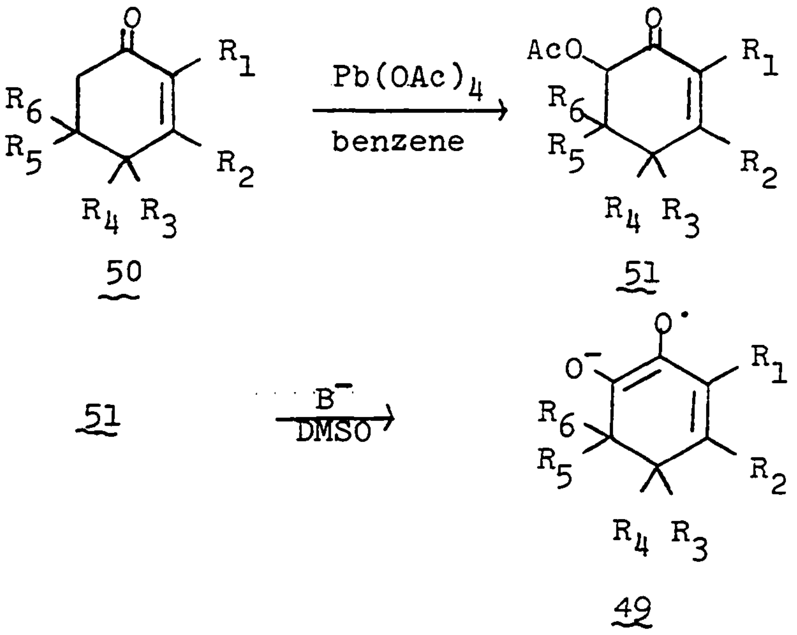
d, $R_1=R_2=R_5=R_6=H$
$R_3=R_4=CH_3$

e, $R_1=R_2=R_5=R_6=H$
$R_3=R_4=C_6H_5$

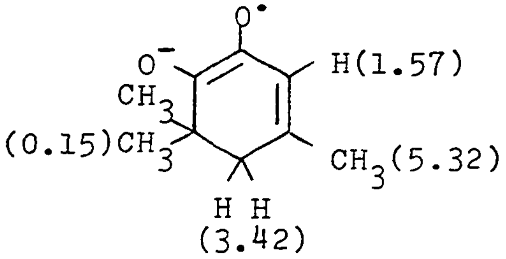
yield of 51a. The reaction of 50b - 50e with $Pb(OAc)_4$ under similar conditions gave 51b - 51e in yields (determined from the NMR's of the crude reaction mixtures) that are given in Table 4. The reaction of 51 with basic DMSO did give rise to the formation of 49.

Table 4. Yields (%) of 51 from the reaction of 50 with $Pb(OAc)_4$

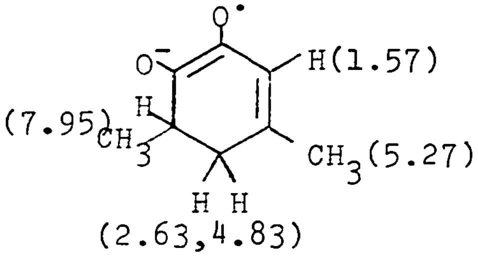
51	Yield (*cis*:*trans*)
b	65 (1:1)
c	85
d	61
e	50



Both 51a and 51b (*cis* and *trans* mixture) reacted with an equimolar amount of potassium t-butoxide in DMSO under static conditions to give 49a and 49b, respectively. The ESR spectra of 49a (Figure 8) and 49b (Figure 9) gave evidence of only a very slow decay in DMSO at room temperature.



49a

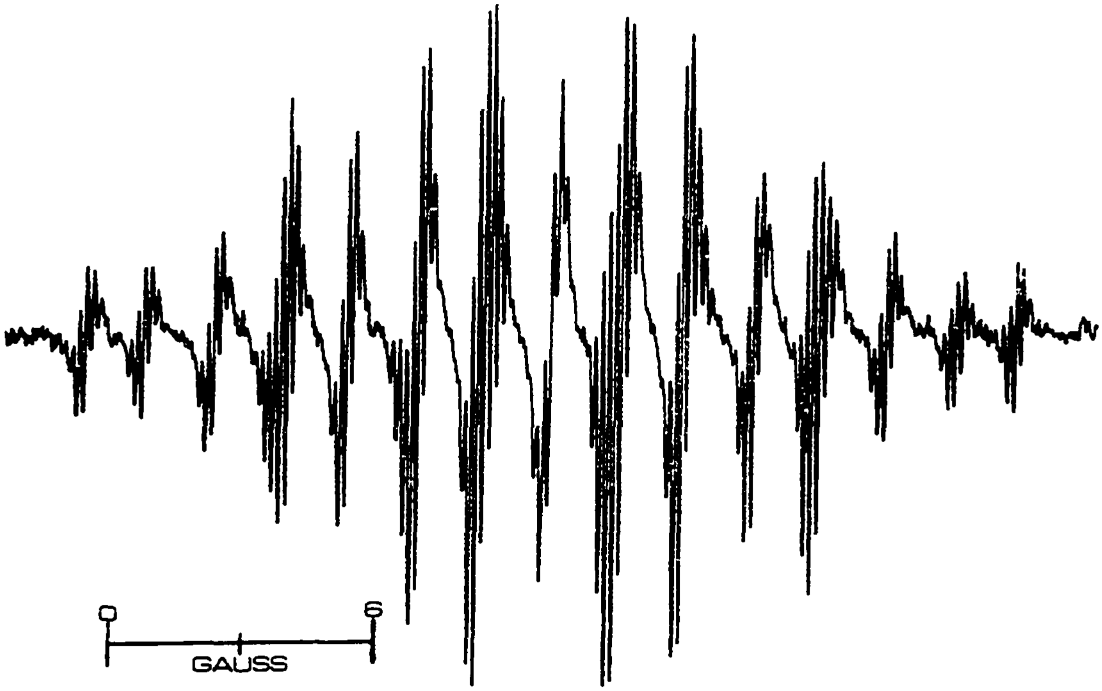


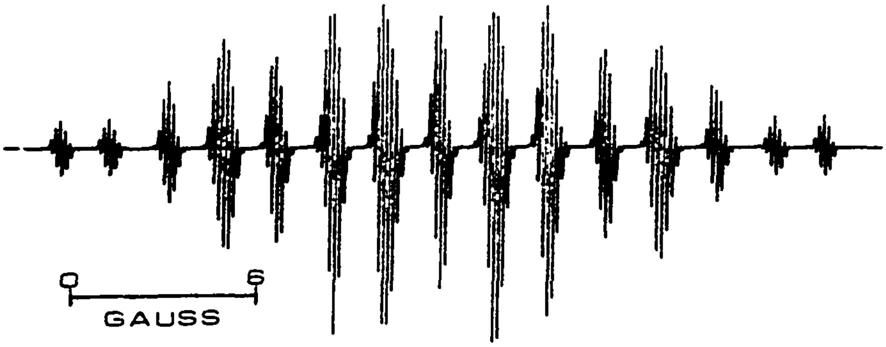
49b

In analogy to the ketyls (with the exception of tropone ketyl) the spin density at the carbon β to the spin label ($\sim$5 gauss) is significantly higher than the spin density at the α-carbon (1-2 gauss). The difference in hfsc's for the hydrogens at C-5 in 49b arises from their magnetic non-equivalence. The rather high splitting constant for the C-6 hydrogen in 49b (7.95 G) results from the presence of the bulky methyl group on the same carbon which forces the hydrogen to spend more time in the quasi-axial position. This gives a decreased dihedral angle and consequently a higher coupling constant.

Reaction of 51c with basic DMSO surprisingly gave the very unstable unsaturated semidione, 49c, as evidenced by its ESR spectrum (Figure 10) recorded under static conditions. The assignment of hfsc's is in good agreement with both 49a and 49b. At this point it appeared that methyl-substitution

Figure 8. The first derivative ESR spectrum of 4,6,6-trimethyl-3-cyclohexene-1,2-semidione, 49a, (top) in DMSO; calculated spectrum (bottom) for Lorentzian linewidth 0.05 gauss and splitting constants from text performed by JEOLCO JNM-RA-1 spectrum accumulator


0
6
GAUSS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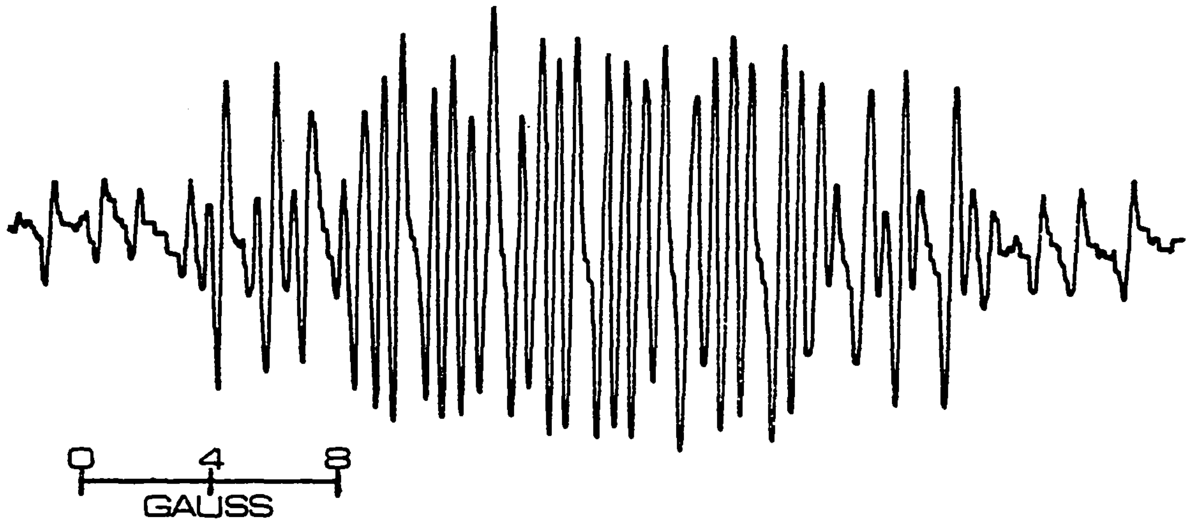
6
GAUSS

Figure 9. The first derivative ESR spectrum of 4,6-dimethyl-3-cyclohexene-1,2-semidione, 49b, (top) in DMSO; calculated spectrum (bottom) for Lorentzian linewidth 0.39 gauss and splitting constants from text performed by JEOLCO JNM-RA-1 spectrum accumulator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4
8
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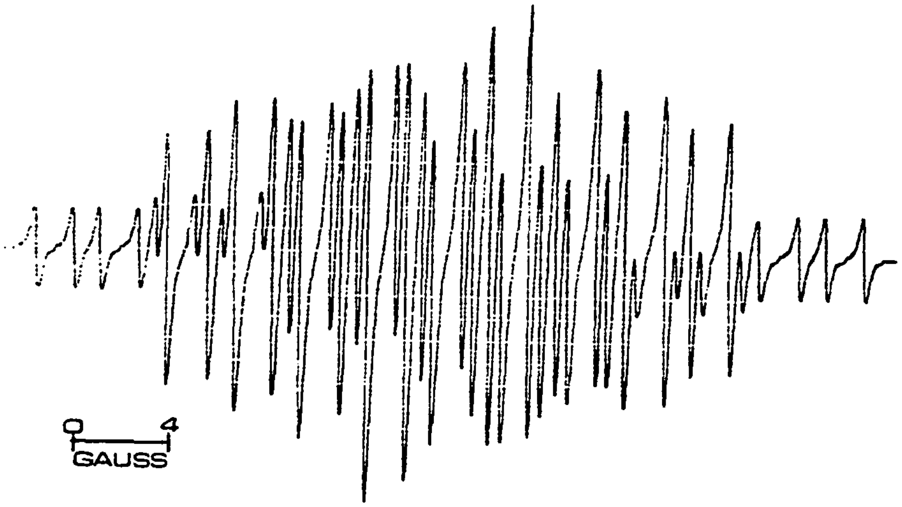
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4
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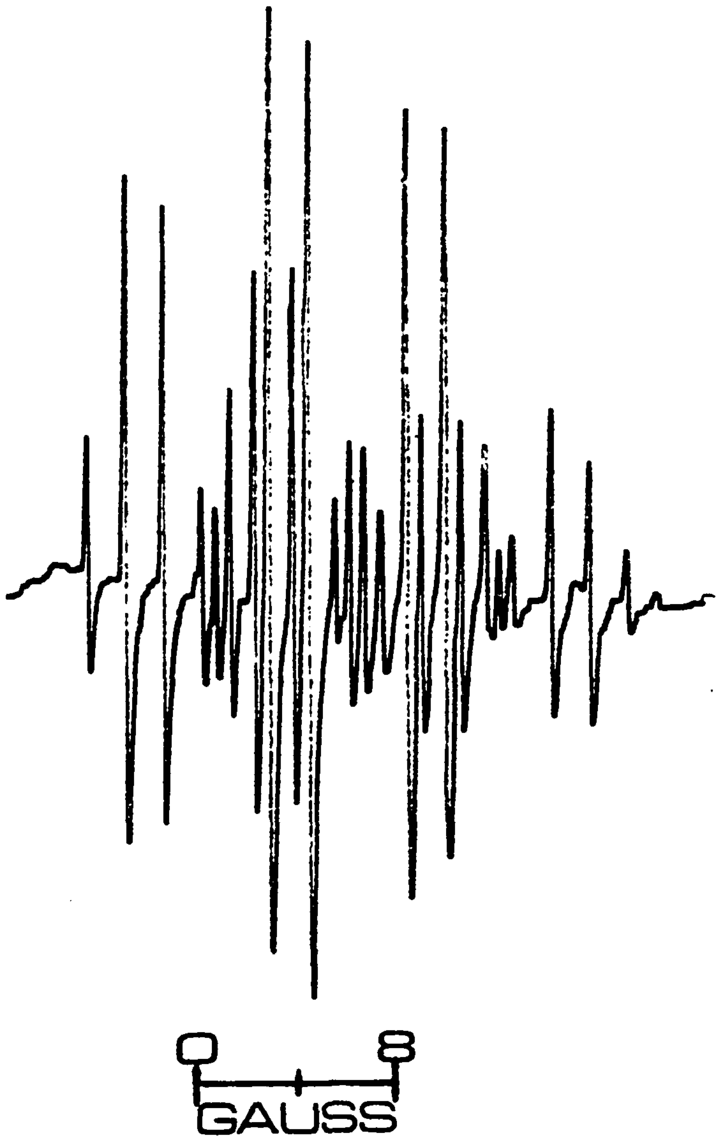
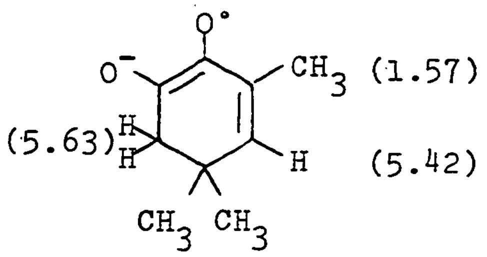
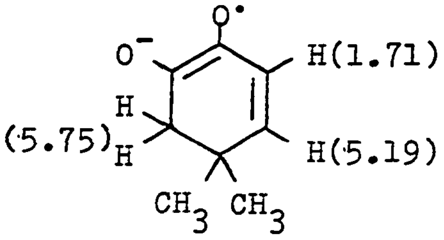


Figure 10. The first derivative ESR spectrum of 3,5,5-trimethyl-3-cyclohexene-1,2-semidione, 49c, in DMSO

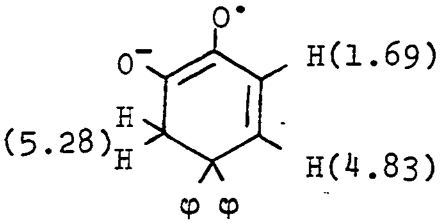


49c

at the C-4 and C-6 positions in 49 was necessary for stabilization. Further support for this observation came from the conversion of 51d to 49d. No ESR signal for 49d was detected upon dissolving 51d in basic DMSO under static conditions. However, when a solution of 51d in DMSO (0.05 M) was allowed to mix with a solution of potassium t-butoxide in DMSO (0.05 M) under flow conditions where the time interval between mixing and detection was about five seconds, the ESR spectrum (Figure 11) of 49d was recorded. The assignment of hfsc's is consistent with 49a - 49c. Replacement of the geminal methyls at C-5 with phenyl groups resulted in enhanced stability since 49e could be observed statically in basic DMSO. The spectra of both 49d and 49e (Figure 12) indicate the presence of a minor amount of a second radical.



49d



49e

Figure 11. The first derivative ESR spectrum of 5,5-dimethyl-3-cyclohexene-1,2-semidione, 49d, in DMSO. The stick diagram indicates the lines assigned to 49d

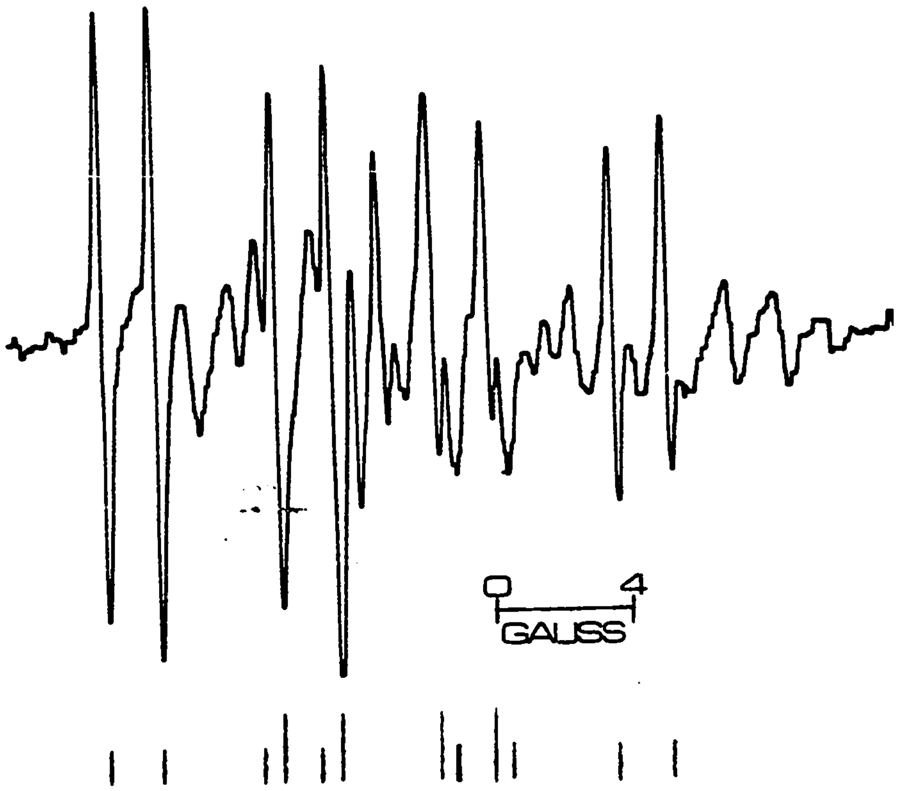
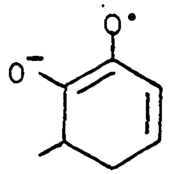


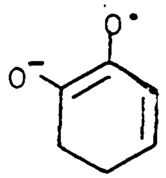
Figure 12. The first derivative ESR spectrum of 5,5-diphenyl-3-cyclohexene-1,2-semidione, 49e, in DMSO. The stick diagram indicates the lines assigned to 49e

The reaction of 51e with varying amounts of base in DMSO gave spectral evidence for at least three different radicals in addition to 49e. No attempt was made to assign structures to these radicals.

The observation that both C-4 and C-6 methyl-substitution in 49 is required for significant stability of the unsaturated semidione was further substantiated by the failure to observe both 52 and 53 with ESR spectroscopy in the reaction of their corresponding acetoxy ketones with basic DMSO under flow conditions. Apparently, if 52 and 53 are formed under these conditions, they are very unstable and decay before detection is possible.

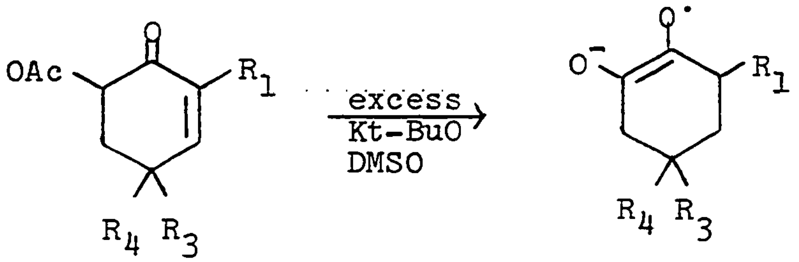


52



53

In addition to a significant difference in stabilities between the C-4 and C-6 methyl-substituted and unsubstituted unsaturated semidiones in the six-membered ring, a second contrast in behavior was also observed. While 51a and 51b reacted with an excess of potassium t-butoxide in DMSO to give only their corresponding unsaturated semidiones; 51c, 51d and 51f gave (under similar conditions) about ten minutes after mixing the ESR spectra of the saturated semidiones,

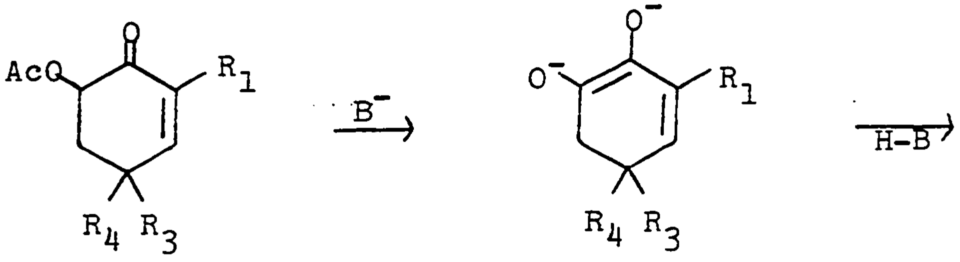


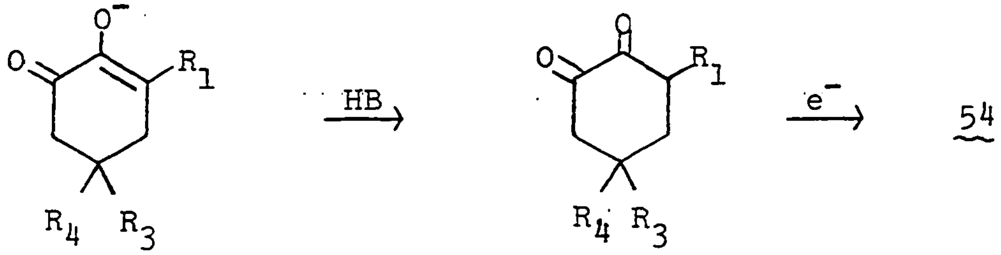
51 **54**

c, R_1=R_3=R_4=CH_3
d, R_1=H; R_3=R_4=CH_3
f, R_1=R_3=R_4=H

54c (Figure 13), **54d** (3), and **54f** (1), respectively. The hfsc's obtained from the spectrum in Figure 13 are consistent with a^H = 5.87 (1H), 11.00 (1H), and 12.70 (1H) G. The assignment of this radical to structure **54c** was made by comparison to **54** (R_1 = CH_3; R_3 = R_4 = H) where hfsc's with a^H = 8.56 (1H), 10.29 (1H) and 11.15 (1H) G have been observed (3). A reasonable mechanism for the conversion of the acetoxy ketones to the saturated semidiones is given in Scheme III. The protonation of the dianion at C-4 would be

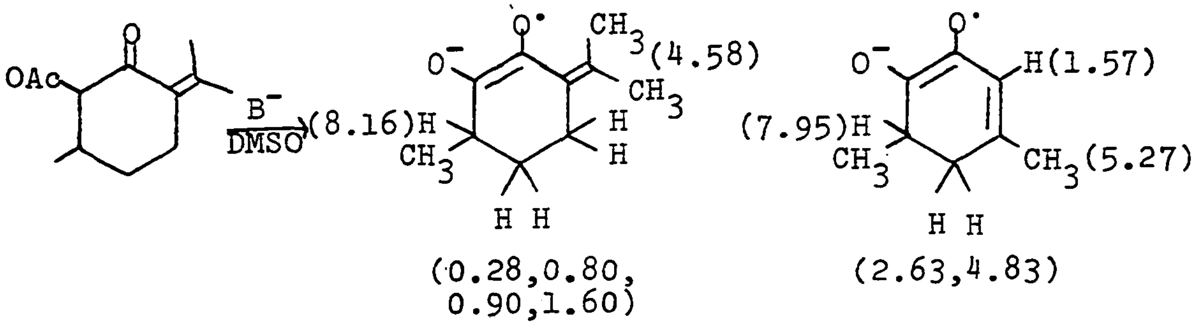
Scheme III





less favorable if a methyl group were present at that position since a tertiary carbanion would be involved. This possibly accounts for both the higher stabilities of the C-4 and C-6 methyl-substituted unsaturated semidiones and their failure to form the saturated semidiones.

Interestingly, when the double bond conjugated to the semidione in the six-membered ring was located in an exocyclic manner, the resulting unsaturated semidione was comparable in stability and in spin density distribution to its endocyclic analog, 49. For example, 55 was prepared from the acetoxy ketone (cis and trans mixture) by dissolution into basic DMSO under static conditions and gave an ESR spectrum

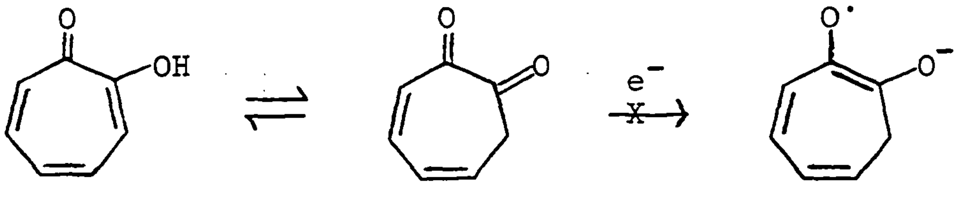


55 49b

Figure 13. The first derivative ESR spectrum of 3,5,5-trimethylcyclohexane-1,2-semidione, 54c, in DMSO

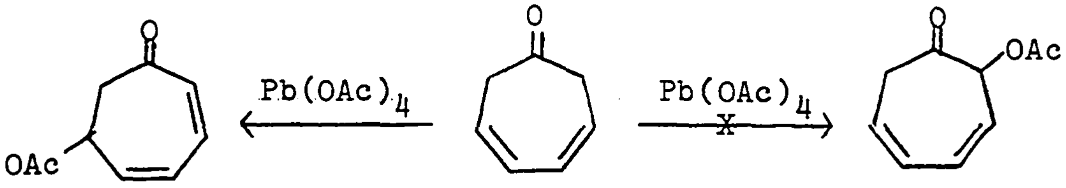
(Figure 14) that gave evidence of only slow decay. In view of its methyl-substitution, 55 can be compared to 49b. Similarities both in stabilities and hfsc's are observed for 49b and 55.

An attempt to generate the doubly unsaturated 1,2-semidione in the seven-membered ring, 56, by reduction of α-tropolone *via* its diketone tautomer with basic DMSO under



56

flow conditions failed. The attempted synthesis of 57 as a second possible precursor to 56 was also unsuccessful. The reaction of 3,5-cycloheptadienone with lead tetraacetate at

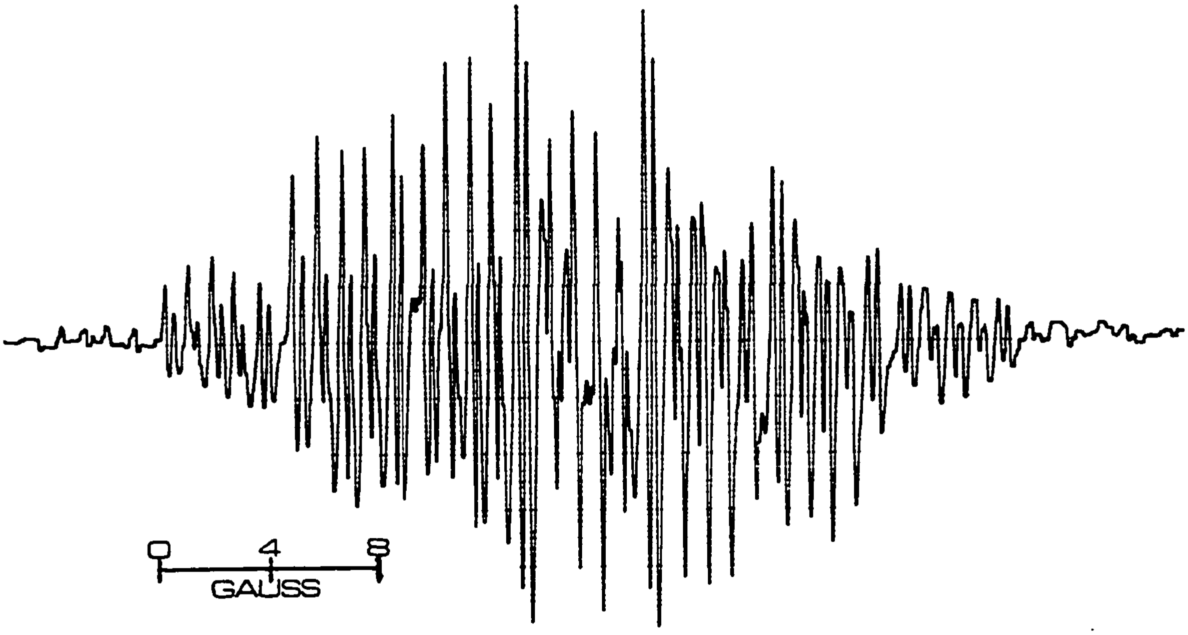


58

57

room temperature did not give the desired 2-acetoxy-3,5-cycloheptadienone, 57, but if fact gave tropone and an acetoxy ketone for which spectroscopic data was consistent with structure 58. Since ketones are believed to react with lead tetraacetate *via* their enolates (39), 58 possibly re-

Figure 14. First derivative ESR spectrum of 55 (top) in DMSO; calculated spectrum (bottom) for Lorentzian linewidth 0.22 gauss and splitting constants from text performed by JEOLCO JNM-RA-1 spectrum accumulator


0
4
8
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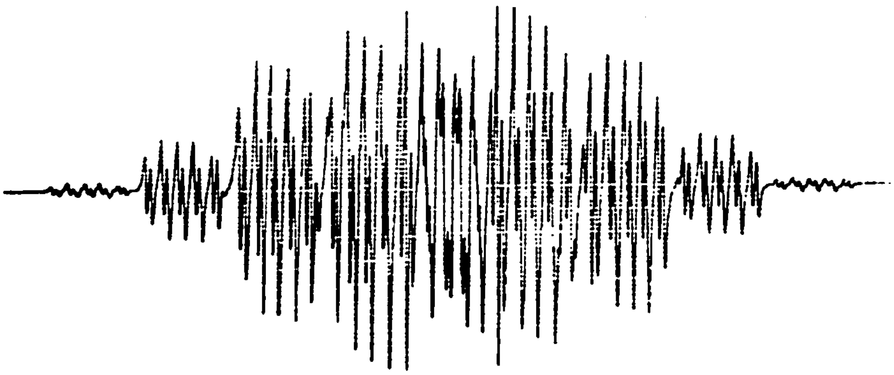
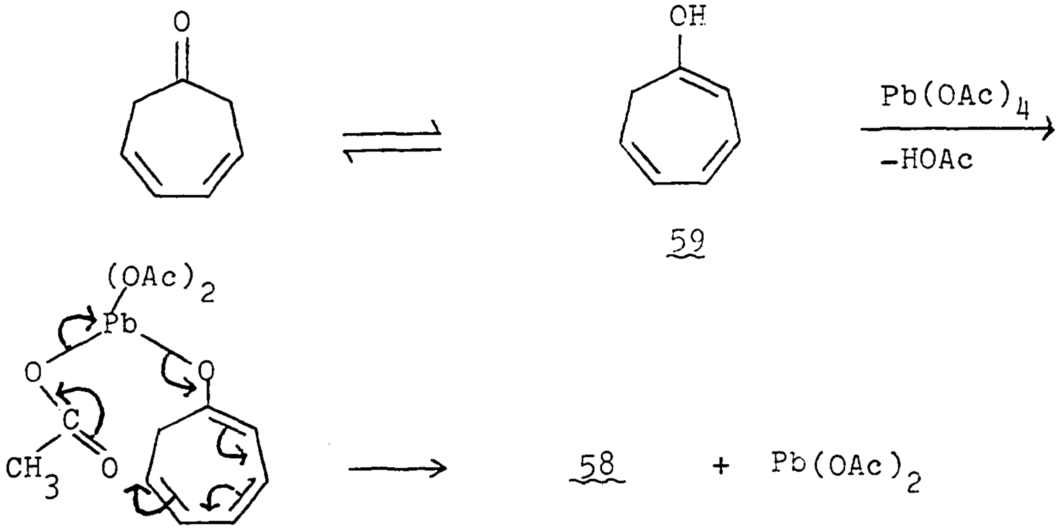
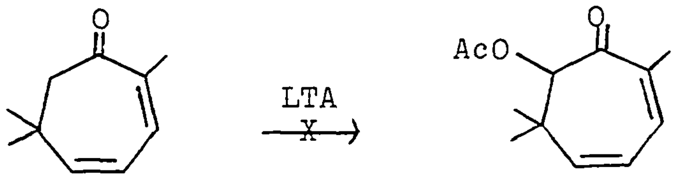


sults from the reaction of 59 with Pb(OAc)$_4$ to form the lead ester followed by the cyclic decomposition of this ester at C-6 as shown in Scheme IV.

Scheme IV



A final attempt to generate the 1,2-semidione in the doubly unsaturated seven-membered ring involved the reaction of eucarvone, 60, with lead tetraacetate (LTA). It was hoped that oxidation would occur at the C-7 position to give 61. The product formed, however, was the acetoxy ketone of



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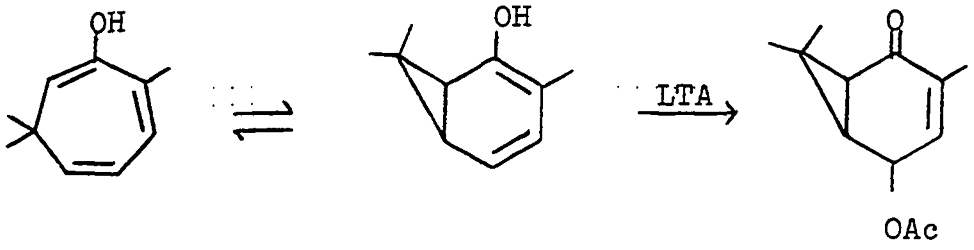
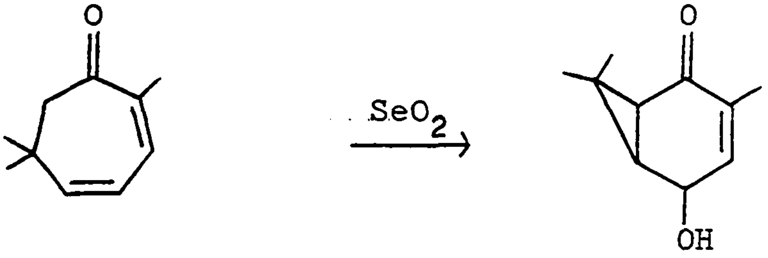
61



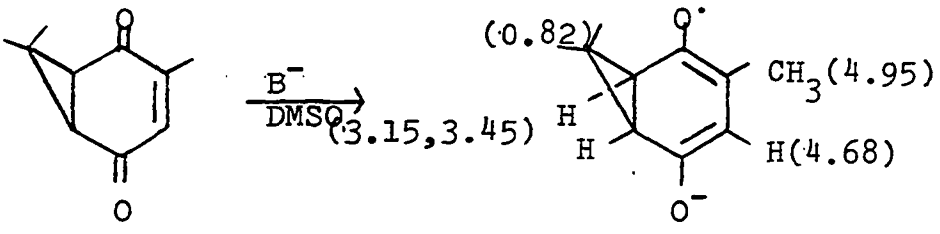
63 62

the bicyclic compound, 62 (only one isomer), which presumably arises from the oxidation of the enol form of the valence isomer of eucarvone, 63. Corey and Burke (40) have also observed the formation of the bicyclic oxidation product, 64, from the reaction of eucarvone with selenium dioxide.



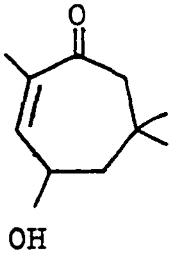
64

Russell and co-workers (11) have observed 3,7,7-trimethylbicyclo[4.1.0]heptene-2,5-semidione, 65, by the treatment of 66 with potassium t-butoxide in DMSO. Surprisingly, dissolution of 62 in basic DMSO produced a radical whose ESR



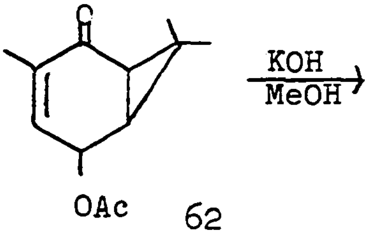
66 65

spectrum (Figure 15) was consistent with a^H = 2.76 (1H), 4.98 (3H), and 2.00 (4H) G and thus eliminated 65 as the structure of the radical. The ESR spectrum recorded for this radical in DMSO-d_6 is shown in Figure 16. The analysis of this spectrum is consistent with a deuterium exchange for all the hydrogen nuclei with the exception of those giving the 4.98 gauss coupling: a^H = 4.98 G (3H); a^D = 0.28 (1D), and 0.41 (4D) G. The radical in Figure 15 has also been observed in these laboratories (35) by treating 67 (41) with basic DMSO.



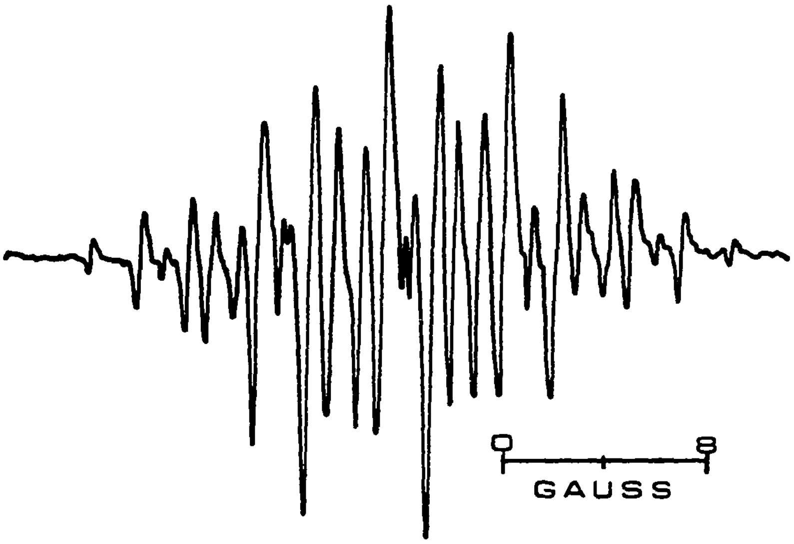
67

In an attempt to assign a structure to this radical, 62 was reacted with two equivalents of KOH in methanol under reflux. In addition to a 45% yield of the hydrolysis product 64, a 3% yield of 2,6,6-trimethylcyclohept-2-en-1,4-dione, 68, and approximately 0.3% yields of both 66 and 69 were



62

Figure 15. The first derivative ESR spectrum of 2,6,6-trimethyl-2-cycloheptene-1,4-semidione, 70, (top) in DMSO; calculated spectrum (bottom) with Lorentzian linewidth 0.45 g and splitting constants from text performed by JEOLCO JNM-RA-1 spectrum accumulator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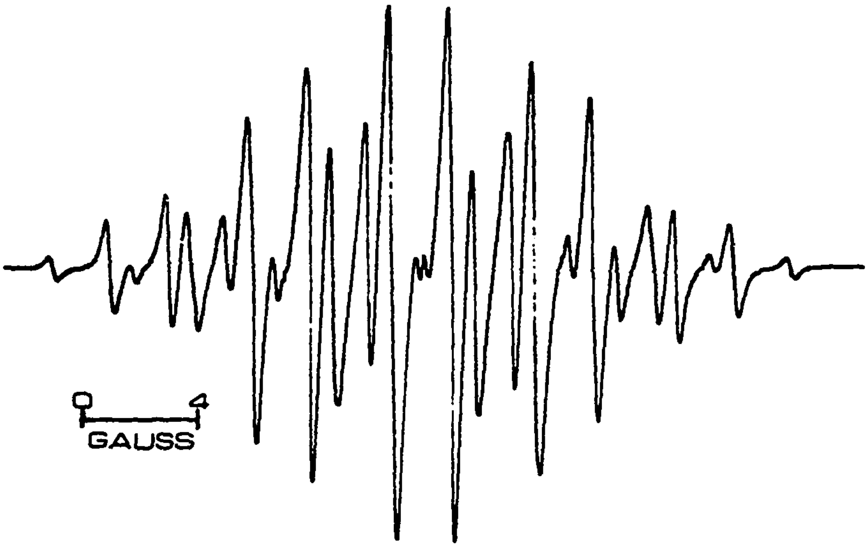
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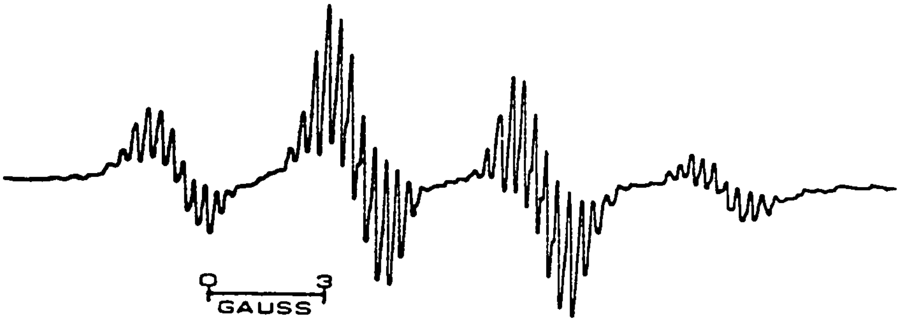
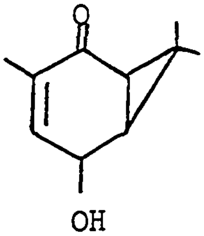


Figure 16. The first derivative ESR spectrum of 2,6,6-trimethylcycloheptene-1,4-semidione, 70, in DMSO-d_6



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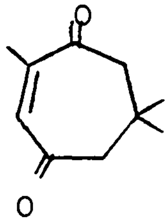

68

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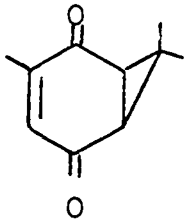
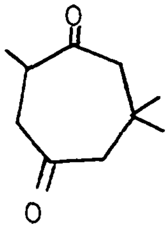


66

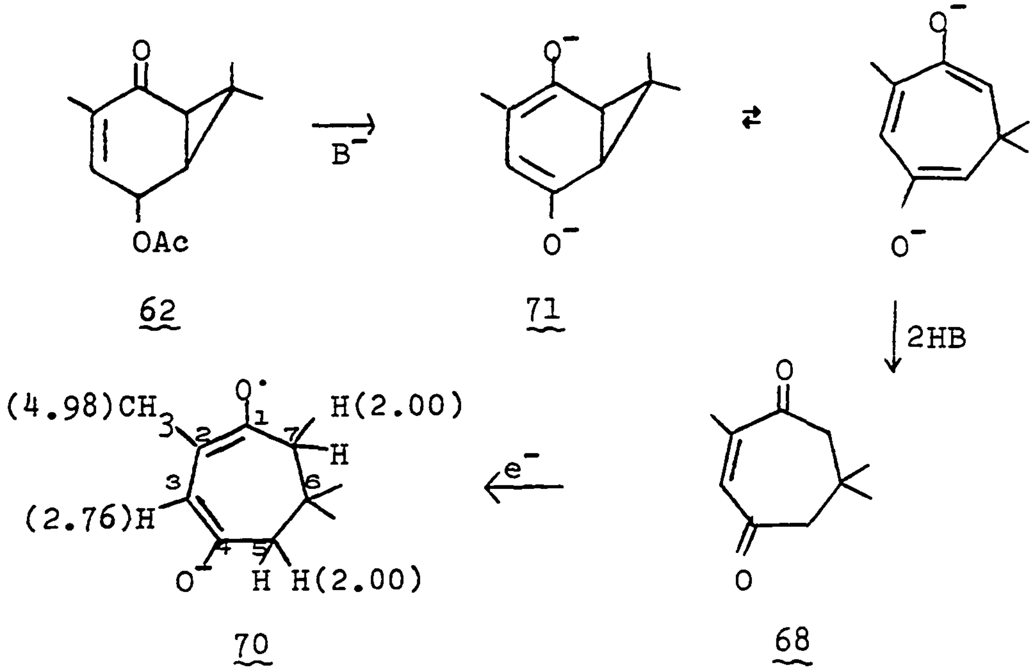
+



69

obtained (products were separated and isolated by preparative glc). In view of the results obtained for 67, and since it is reasonable that 68 might be formed from 62 in basic DMSO, the radical was assigned structure 70, the one electron reduction product of 68. The assignment of hfsc's in 70 is consistent with 39 - 41. A rationalization for the formation of 70 from 62 is given in Scheme V.

Scheme V

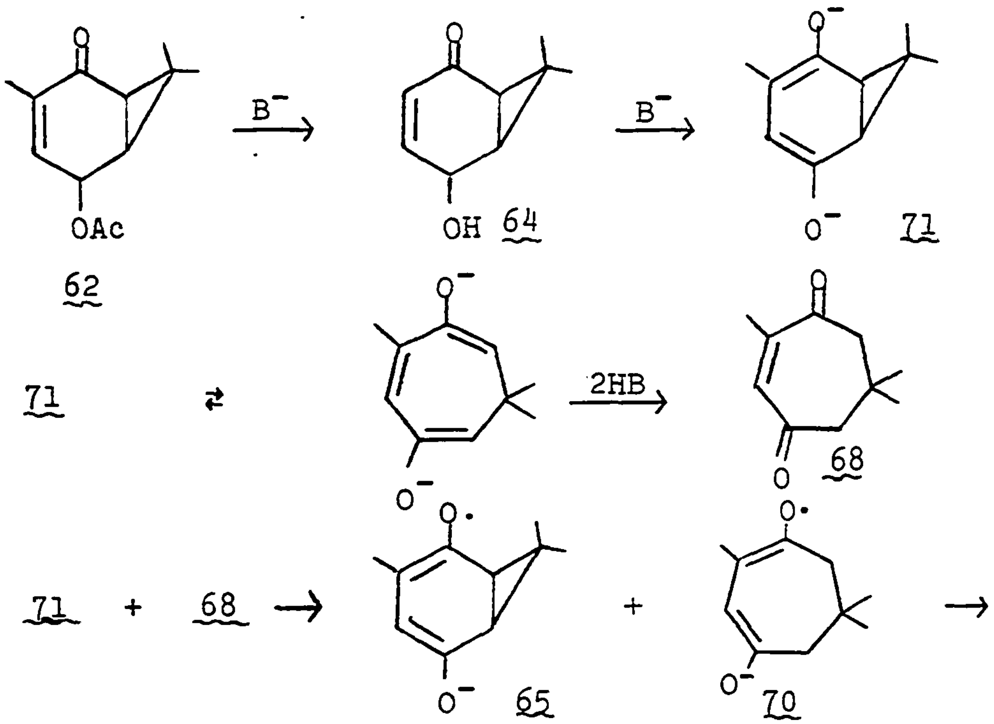


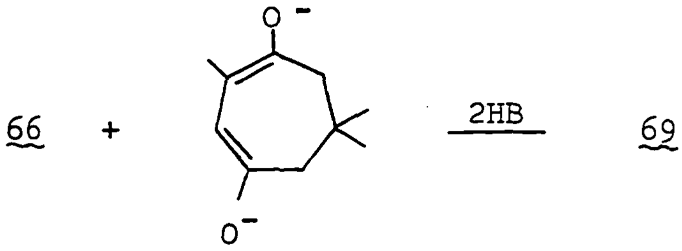
This reaction scheme is consistent with deuterium exchange with basic DMSO-d_6 at C-3, C-5 and C-7. The incorporation of deuterium at C-3 presumably occurs in the dianion 71.

The absence of the bicyclic semidione, 65, in the reaction of 62 with basic DMSO is very surprising since its formation from the oxidation of 71 by 68 would be reasonable. However, dissolution of a mixture of equimolar amounts of 68 and 66 into basic DMSO gave an ESR signal of 70 only. Evidently the reduction potential of 68 is significantly lower than 66. Therefore, if 65 is generated in the presence of 68, electron transfer to 68 occurs to give 66 and 70.

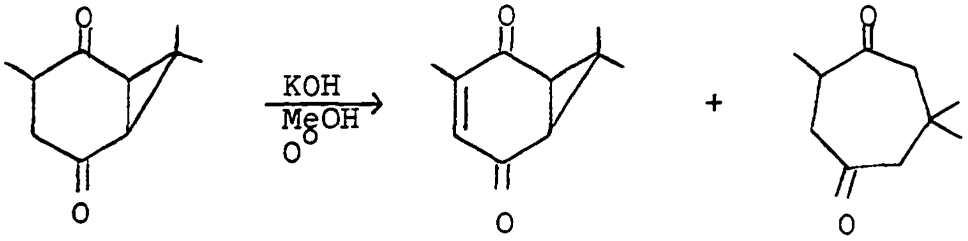
The suggested routes for the formation of 64, 66, 68, and 69 from 62 in basic methanol are given in Scheme VI.

Scheme VI





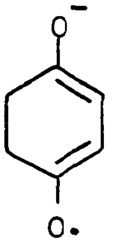
The reduction-oxidation sequence for the formation of 66 and 69 has also been suggested by Wenkert and Yonder (42) in the reaction of the bicyclic diketone, 72, with basic methanol at 0°. In contrast to 62, 72 gave only 66 and 69 in equimolar amounts for a combined yield of 40%. The formation of 68 was not observed.



72 66 69

In contrast to cyclic saturated semidiones which generally are easily formed and possess high stability, the cyclic unsaturated semidiones frequently are unstable and require the use of flow systems as a means of detection. Apparently the presence of the double bond(s) in the molecule gives rise to a labile specie under the conditions necessary for generation of the semidione.

The difference in stabilities between the unsaturated 1,4- and 1,2-semidiones deserves comment. In the six-membered ring this difference is substantial since the 1,4-semidione, 37, is stable for several hours at room temperature while the 1,2-semidione, 53, is not detected without



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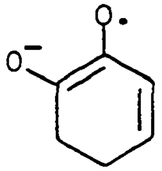
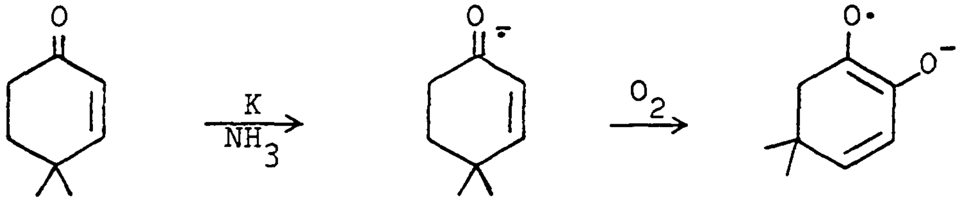


53

alkyl-substitution. This difference is essentially diminished in the five-membered ring where both the 1,4- and 1,2-semidiones have lifetimes in DMSO of about 5-10 seconds. The presence of the double bond external to the spin label in the unsaturated 1,2-semidione may result in an increased susceptibility to nucleophilic attack relative to the internal double bond in the 1,4-semidione.

In view of the results on the unsaturated 1,2-semidiones in the six-membered ring, 49, a report of Chen and Bersohn (43) also deserves comment. Chen and Bersohn reported that the ketyl of 4,4-dimethylcyclohexenone, 73, could be detected at -60 by the reduction of 4,4-dimethylcyclohexenone with potassium in liquid ammonia. The ESR spectrum assigned by Bershon and Chen to the ketyl is identical to the spectrum of 49d shown in Figure 11. Apparently oxygen was present

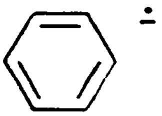


73 49d

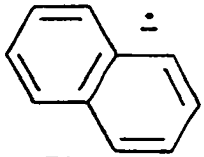
in their system resulting in the oxidation of the ketyl to the semidione.

BENZO DERIVATIVES OF UNSATURATED SEMIDIONES

Benzo-substitution of double bonds in molecules containing an unpaired electron in their π-framework results in a substantial increase in stability. For example, although the radical anion of benzene, 74, can be observed at about -70° (44), an increase in temperature results in its rapid decay. Benzo-substitution of one or two of the double bonds in 74 to give the radical anions of naphthalene, 75, or anthracene, 76, gives increased stability since both



74



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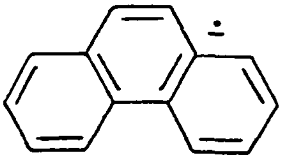
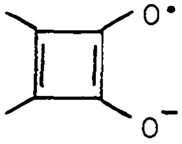


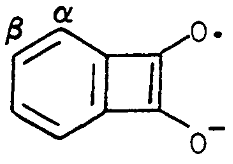
76

75 and 76 can be readily observed at +25° (26). The increased stabilization reflects the increasing delocalization of the unpaired electron in going from 74 to 76.

Benzo-substitution of double bonds in conjugation to semidiones also produces a radical anion with increased stabilization. This observation results from a recent report by Geske and Balch (45). Although various attempts in these laboratories to prepare 42 by the reduction of dimethylcyclobutenedione (electrolytically) were unsuccessful, Geske and Balch were able to observe the benzo derivative, 77, by the electroreduction of benzocyclobutadienoquinone in acetonitrile. They observed hfsc's of



42



77

1.87 and 3.74 G at the α and β-positions, respectively.

Benzo derivatives of the unsaturated 1,4-semidiones in the five-membered ring have also been studied. Electrolytic reduction of 78 produced the radical anions, 79, which gave the hfsc's assigned in Table 5. The assignments of hfsc's

78 79

Table 5. Observed hfsc's (G) of 79

X	Position 4,7	 5,6	Other hfsc's
O[a]	0.27	2.68	
O[b]	0.21	2.55	
S[b]	0.31	2.15	

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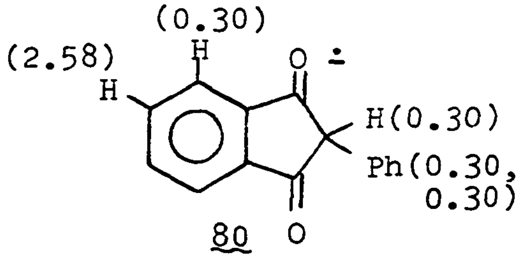
[a] Reference 46.

[b] Reference 47.

Table 5 (Continued)

X =	Position 4,7	 5,6	Other hfsc's
NH^a	0.28	2.65	$a^H = 2.54$, $a_{NH}^H = 0.46$
NH^b	0.24	2.40	$a^N = 2.40$, $a_{NH}^N = 0.41$
CH^{-b}	0.23	2.42	$a_{CH}^H = 0.85$
CCH$_3^{-b}$	0.24	2.54	$a_{CH_3}^H = 1.33$

were in excellent agreement with HMO calculations. In some instances better resolution of spectra was obtained by lowering the temperature to about -40° (46). The ESR spectrum obtained from the reduction of 2-phenylindan-1,3-dione consisted of a 1:2:1 triplet of 2.58 G which was further split, possibly by five nearly equivalent hydrogens (0.30 G). Sioda and Koski assigned structure 80 to this radical (46). In view of the results obtained for both indan-1,3-dione and 2-methylindan-1,3-dione which generate radical dianions when they are reduced electrolytically (47), the radical dianion structure 81 would seem more reasonable than 80.



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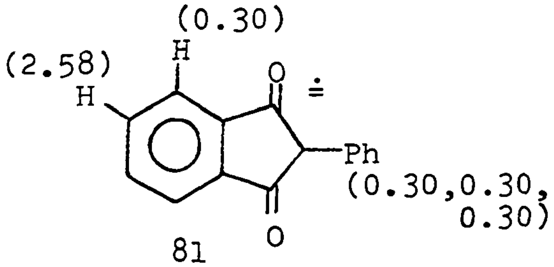
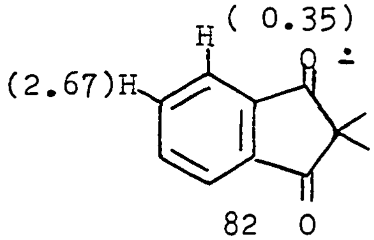


81

Electrolytic reduction of 2,2-dimethylindan-1,3-dione at room temperature[4] produced a poorly resolved ESR spectrum consisting of a broad 1:2:1 triplet of 2.67 G. The assignment of this radical to structure 82 in which the 2.67 gauss coupling arises from the C-5 and C-6 hydrogens appears valid



82

by comparison to 79. The geminal methyl groups in 82 lie in the nodal plane of the highest occupied molecular orbital and consequently would be expected to have low spin densities.

In contrast to 5,5-dimethyl-3-cyclopentene-1,2-semidione, 46, which has a lifetime of only seconds in DMSO at room temperature, Russell and co-workers (48) have observed that indan-1,2-semidione, 83a, is remarkably stable in DMSO solution. Russell and co-workers have also observed 83b - 83k with ESR spectroscopy. The hfsc's obtained from the ESR spectra of 83 are given in Table 6. The larger values of $a_{aromatic}^{H}$ were assigned to the hydrogen atoms at C-5 and C-7 on the basis of their HMO calculations.

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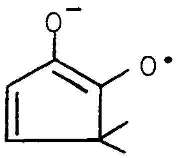
[4] J. Mattox, Iowa State University, Ames, Iowa. Private Communication, 1971.



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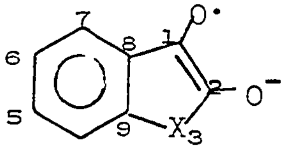


83

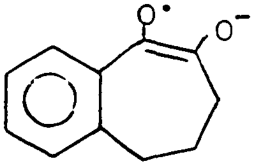
a, X = CH_2
b, X = C=O
c, X = $C(CH_3)_2$
d, X = $C(OCH_3)_2$
e, X = O
f, X = S
g, X = NCH_3
h, X = NH
i, X = N^-
j, X = NOH
k, X = NO^-

Table 6. Hfsc's (G) of 83 in DMSO

X =	$a_{aromatic}^H$	Other hfsc
83a, CH_2	2.95, 2.83, 0.73, 0.56	$a_{CH_2}^H = 2.62$
83b, C=O[a]	0.95, 0.95, 0.95, 0.95	
83c, $C(CH_3)_2$	2.87, 2.75, 0.81, 0.47	$a_{CH_3}^H = 0.33$
83d, $C(OCH_3)_2$	2.45, 2.45, 0.65, 0.13	$a_{CH_3}^H = 0.13$
83e, O	3.44, 3.04, 0.91, 0.91	
83f, S	2.86, 2.43, 0.82, 0.70	
83g, NCH_3	3.86, 2.94, 1.00, 1.00	$a^N = 0.90$, $a_{CH_3}^H = 0.63$
83h, NH	3.73, 3.17, 1.00, 0.92	$a^N = 1.06$, $a_{NH}^H = 0.19$
83i, N^-	4.23, 3.40, 0.99, 0.99	$a^N = 0.53$
83j, NOH	3.74, 2.91, 0.70, 0.70	$a^N=0.35$, $a_{OH}^H=0.33$
83k, NO^-	3.67, 2.74, 1.02, 0.64	$a^N = 0.17$

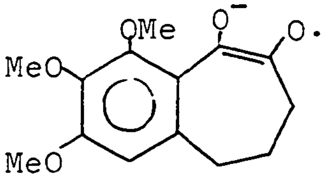
[a] Reference 49.

Several benzo derivatives of unsaturated semidiones in the seven- and eight-membered rings have been prepared in these laboratories. Benzocycloheptanesemidione (50), 84, and two of its derivatives, 85 and 86 (51), were generated by exposing solutions of their corresponding ketones in basic DMSO to oxygen. The largest splitting constant in each of these semidiones is similar in magnitude to the 6.6 G coupling constant observed for two of the α-hydrogens in cycloheptanesemidione (6). The reaction of dibenzo-[a,e]-cyclooctatetraene-5,6-dione with basic DMSO solutions of propiophenone gave the radical anion, 87. No assignments of hfsc's were made (51).



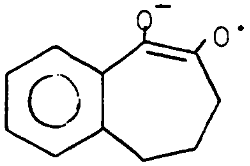
84

a^H = 6.9(H), 2.5(1H), 0.75(2H), 0.30(2H), 0.15 (1H)



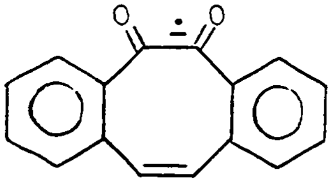
85

6.3(1H)
0.7(3H)



86

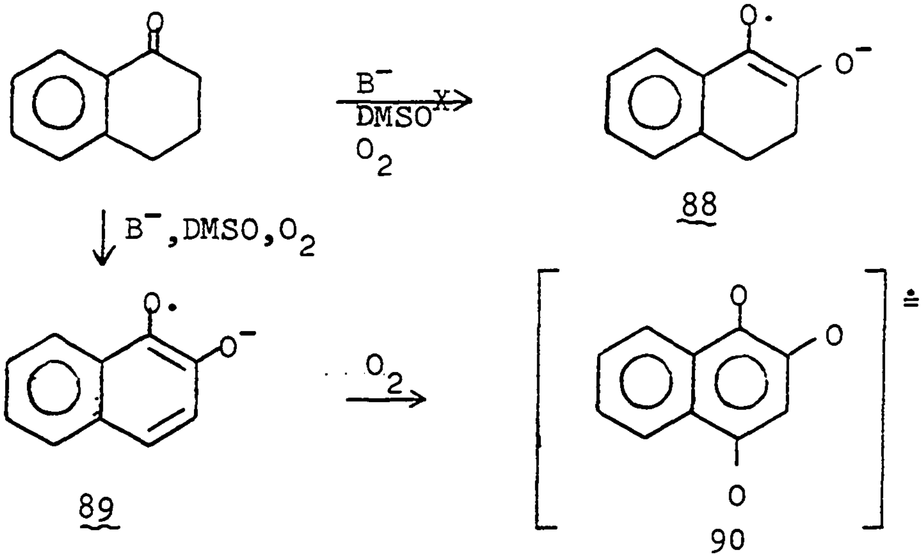
6.3(1H) G
other splittings less than 0.5 G



87

a^H = 0.95(2H), 0.57(6H), 0.38(2H) G

Surprisingly, the addition of oxygen to a solution of α-tetralone in basic DMSO produced a radical which gave an ESR spectrum that was not consistent with the 1,2-semidione 88 (51). The ESR signal of this radical rapidly decayed and after several minutes was replaced with the spectrum of a different radical which had indefinite stability. Subsequent work (51) revealed that the radical initially formed was o-naphthosemiquinone, 89, which was further oxidized under these conditions to the radical dianion 90.



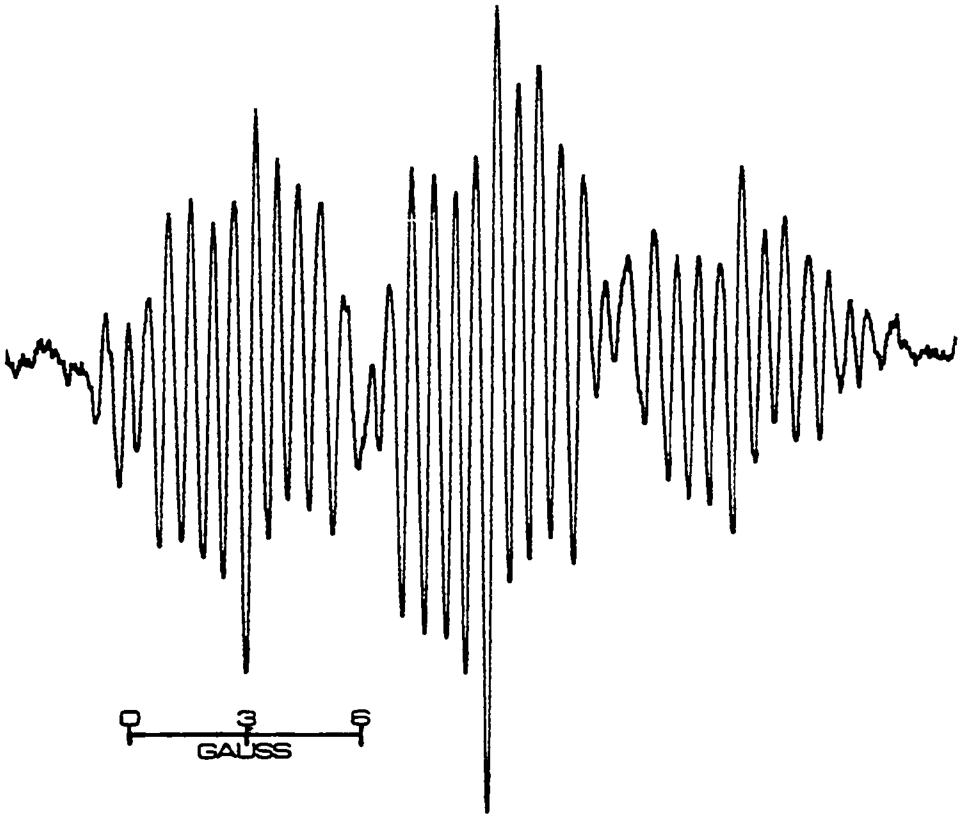
88

89

90

Since acetoxy ketones are in certain instances better precursors to semidiones than monoketones, α-tetralone was reacted with lead tetraacetate to give 2-acetoxy-1-tetralone, 91. The reaction of 91 with basic DMSO in the absence of oxygen under static conditions produced a radical which gave the ESR spectrum shown in Figure 17. Exposure of this solution to air resulted in the formation of the radical dianion 90. The spectrum in Figure 17 consists of a 1:2:1 triplet of 6.33 G which is further resolved into smaller hfsc's. This radical was assigned to the structure of the semidione 88.

Figure 17. The first derivative ESR spectrum of tetralin-1,2-semidione, **88**, (top) in DMSO; calculated spectrum (bottom) with Lorentzian linewidth 0.45 gauss and splitting constants from text performed by JEOLCO JNM-RA-1 spectrum accumulator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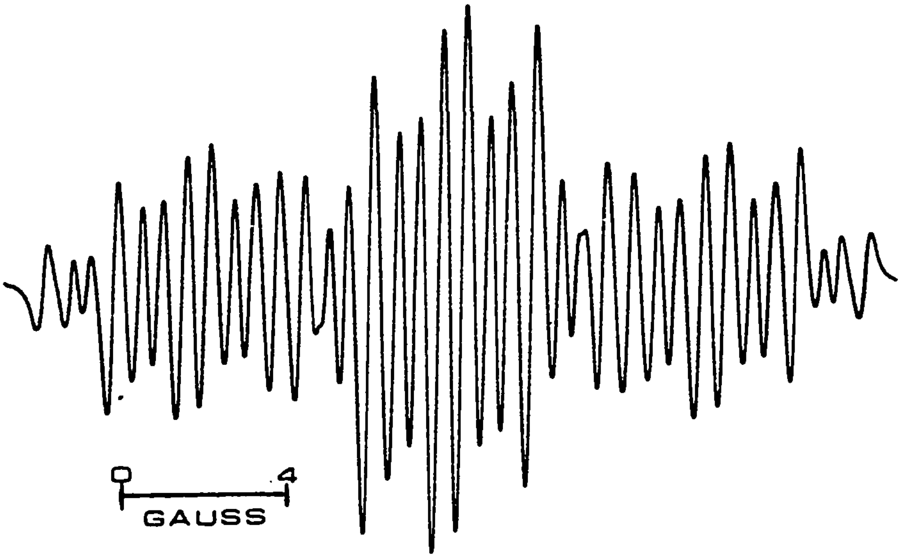
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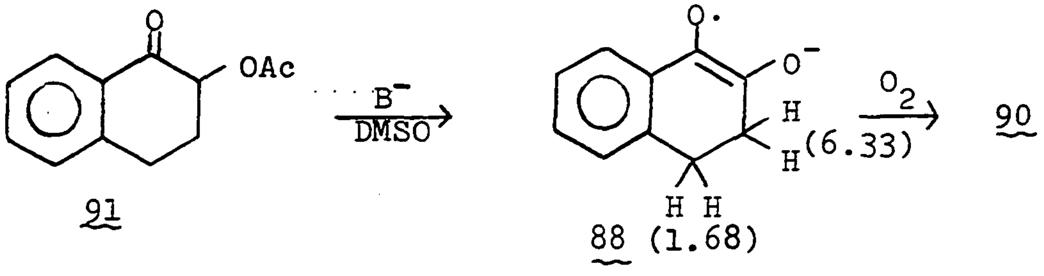
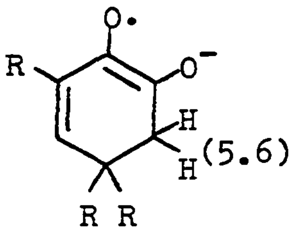
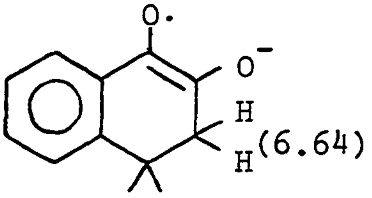


$a_{\text{aromatic}}^{H} = 2.23, 1.08, 0.65, 0.40$

Support for this assignment is two-fold. First, the methylene hydrogens α to the semidione in **88** give a hfsc of 6.33 G which is similar in magnitude to the 5-6 G hfsc's observed for the analogous hydrogens in **49**. Secondly, Strom et al. (52) have recently reported their preparation of the 4,4-dimethyl derivative of **88**, **92**, in which they observed a 6.64 G coupling constant for the methylene hydrogens α to the semidione.



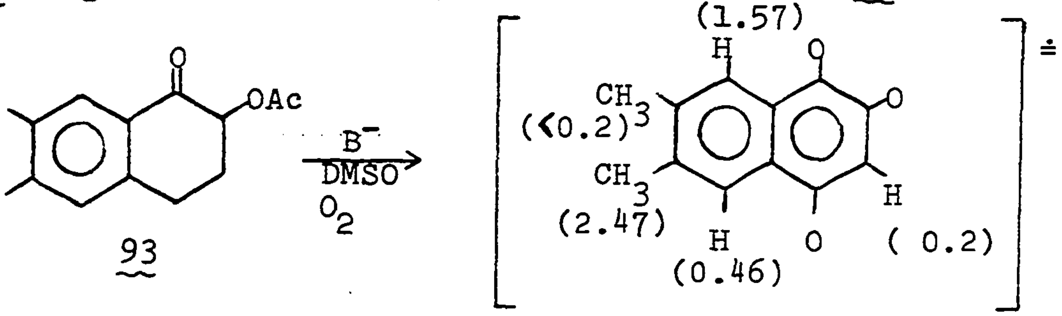
49



92

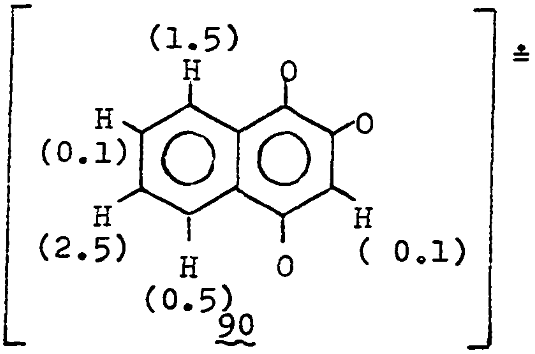
$a_{\text{aromatic}}^{H} = 2.42\ (2H),\ 0.68\ (2H)$

Strangely, the reaction of 2-acetoxy-6,7-dimethyl-1-tetralone, **93**, with basic DMSO in the absence of oxygen either statically or under flow conditions produced a radical which gave a weak unresolved spectrum. The failure of **93** to produce an appreciable amount of the 6,7-dimethyl derivative of **88** is certainly unexpected. However, **93** could be oxidized to the radical dianion, 94, in analogy to the acetoxy ketone 91. The hfsc's obtained from the ESR spectrum of 94 (Figure 18) were assigned by comparison to 90.



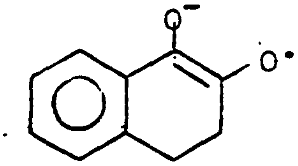
93

94

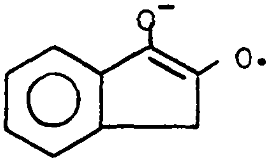


90

Although 88 could be generated in sufficient yields for its detection, its ESR spectrum gave evidence (Figure 17) of not only a weak signal but also of a slow decay. This is somewhat in contrast to 83a which was found to be quite stable and could even be observed in aqueous solution (48).



88



83a

Since it was also of interest to know if this contrast existed for the heteroatom derivatives, 95a - 95f were prepared and observed with ESR spectroscopy.

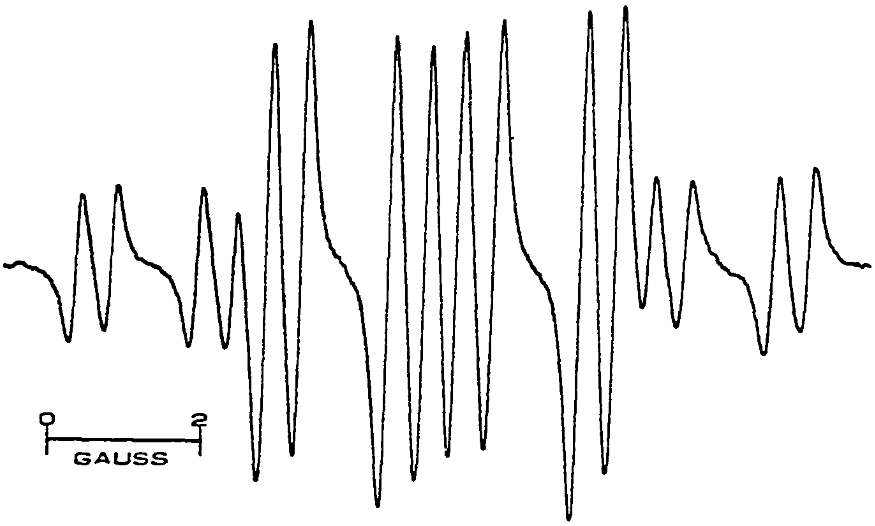
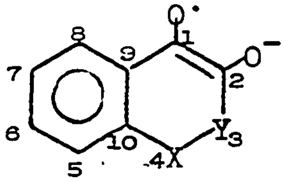


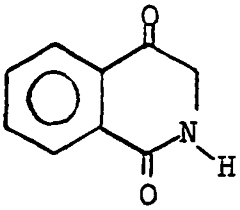
Figure 18. The first derivative ESR spectrum of the radical dianion, 94, in DMSO



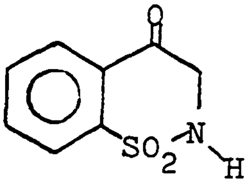
95

a, X = C=O; Y = N^-
b, X = SO_2; Y = N^-
c, X = SO_2; Y = CH^-
d, X = SO_2; Y = CD^-
e, X = O; Y = CH_2
f, X = S; Y = CH_2

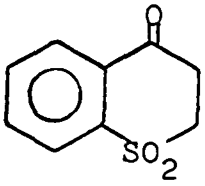
The addition of air to basic DMSO (DMSO-d_6) solutions of 1,2,3,4-tetrahydroisoquinoline-1,4-dione, 96, and 2H-1,2-benzothiazin-4(3H)-one 1,1-dioxide, 97, and basic DMSO solutions of thiochroman-4-one 1,1-dioxide, 98, produced radicals which gave the ESR spectra shown in Figures 19, 20, and 21, respectively. Similar treatment of 98 in basic DMSO-d_6 produced a radical which gave the ESR spectrum also shown in Figure 21. These radicals were obtained in good yields and were stable for several hours at room temperature in DMSO. Addition of more oxygen destroyed these radicals and in the case of 97 resulted in the formation of several different radicals to which structures were not assigned. On the basis of the hfsc's which were obtained from the



96

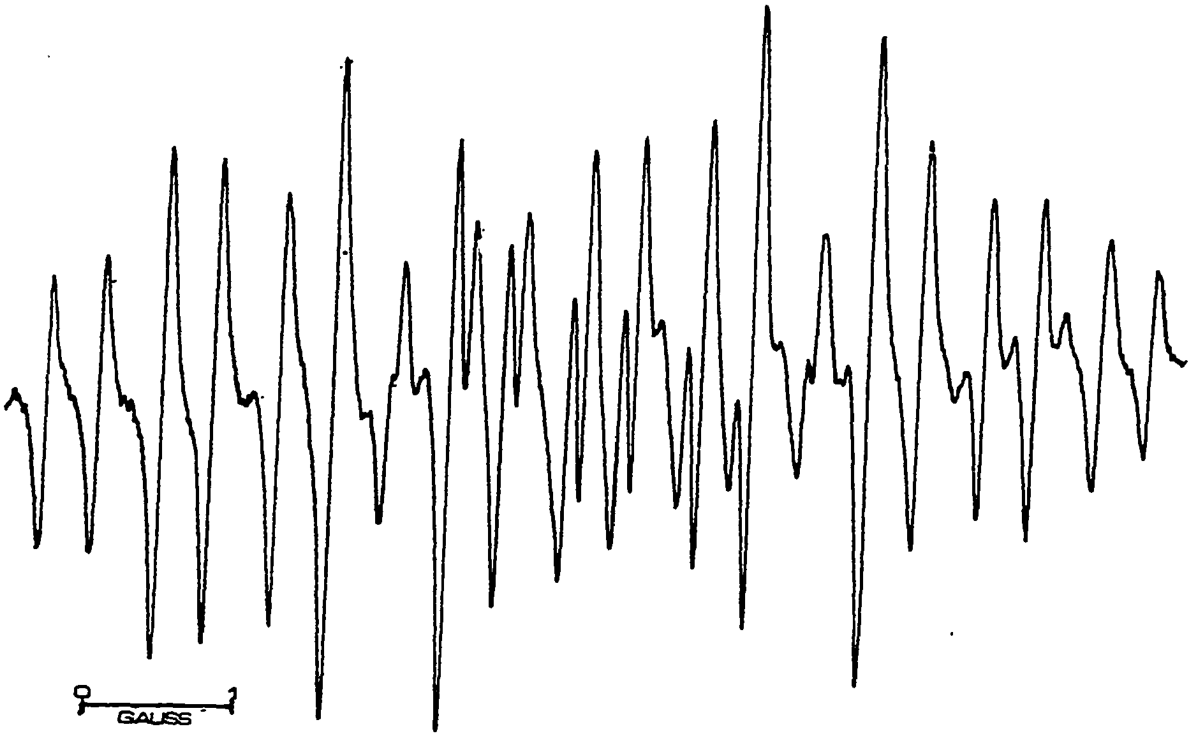


97



98

Figure 19. The first derivative ESR spectrum of 95a (top) in DMSO; calculated spectrum (bottom) with Lorentzian linewidth 0.10 gauss and splitting constants from text performed by JEOLCO JNM-RA-1 spectrum accumulator


0
1
GAUSS

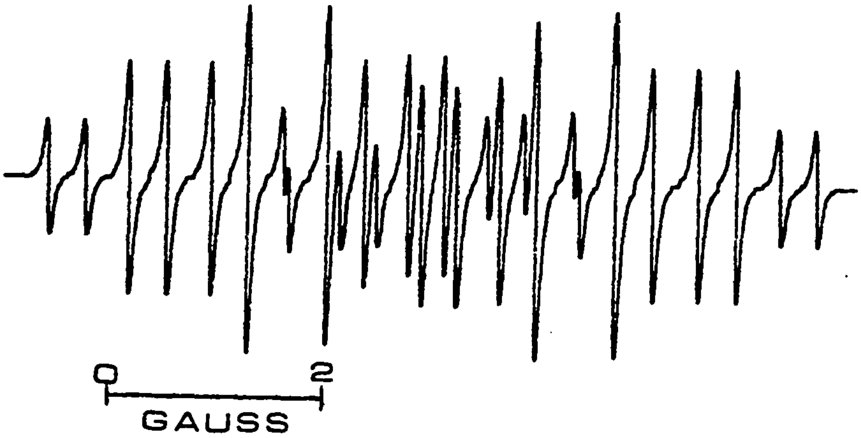
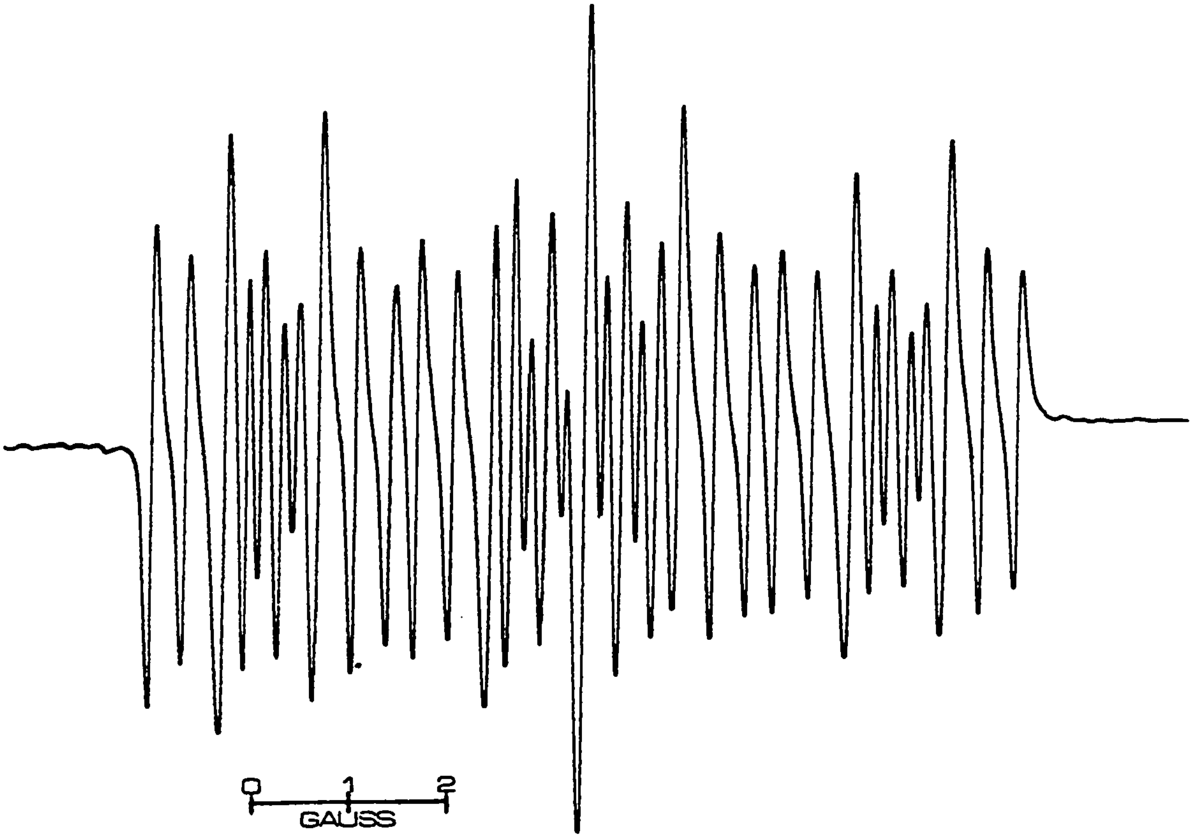

0
2
GAUSS

Figure 20. The first derivative ESR spectrum of 95b (top) in DMSO; calculated spectrum (bottom) with Lorentzian linewidth 0.15 gauss and splitting constants from text performed by JEOLCO JNM-RA-1 spectrum accumulator


0
1
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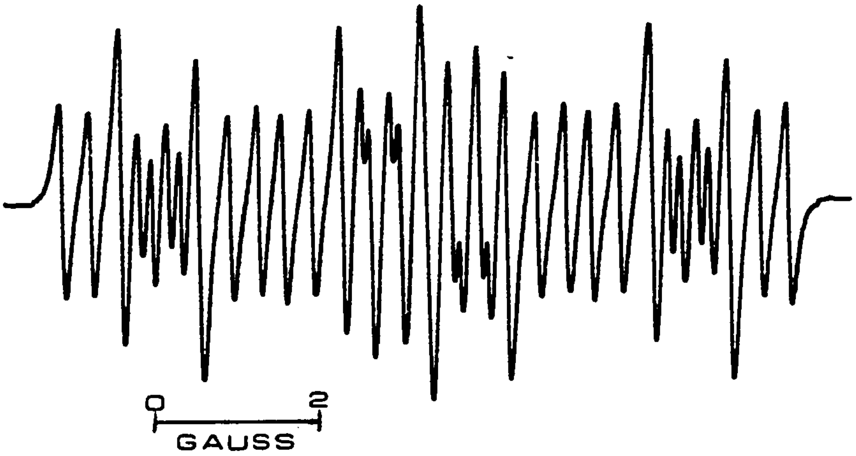
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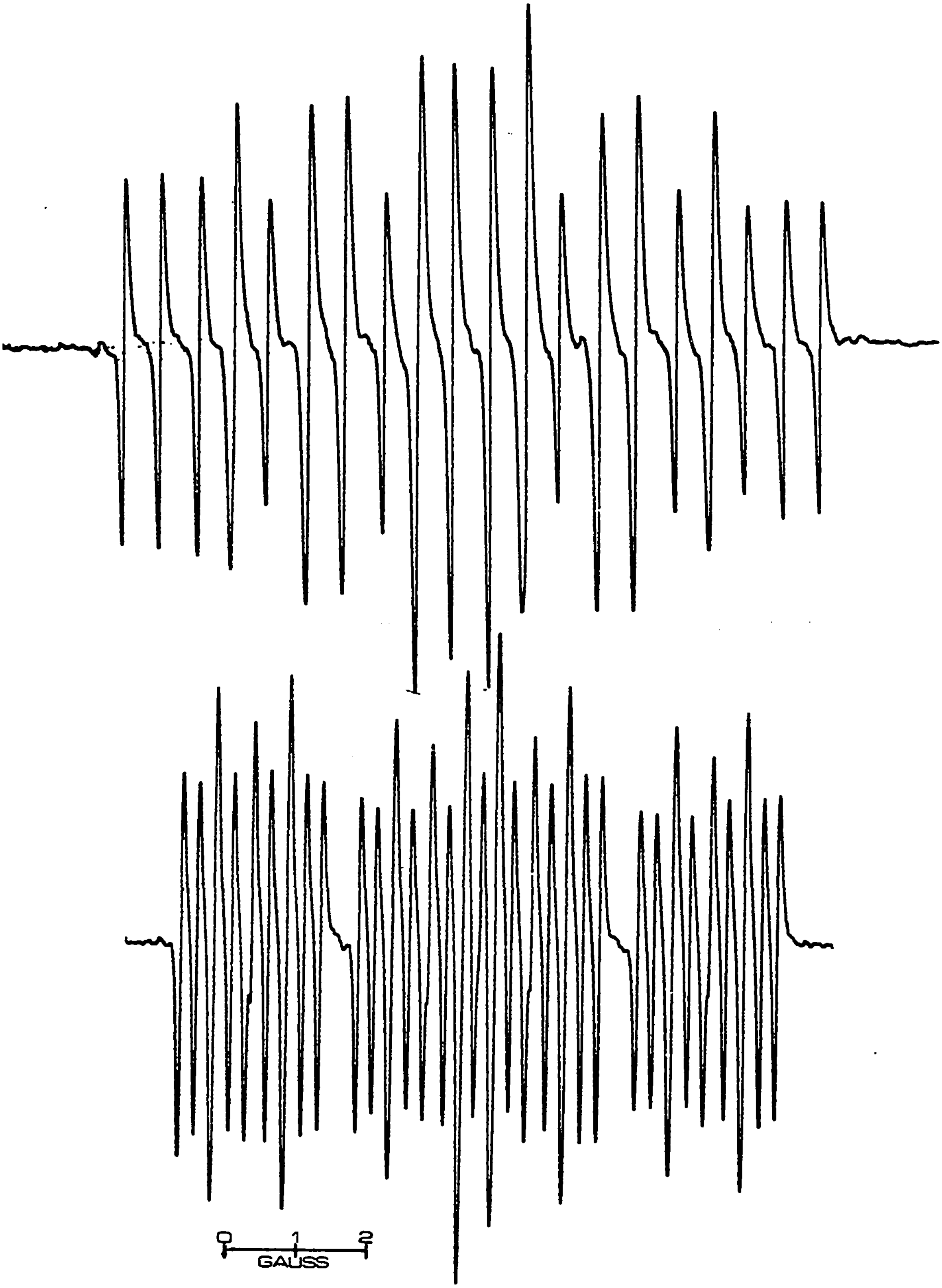
GAUSS

Figure 21. First derivative ESR spectra of 95c in DMSO (top) and of 95d in DMSO-d_6 (bottom)


0
1
2
GAUSS

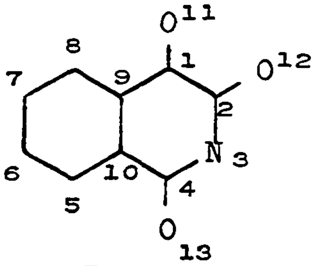
the spectra in Figures 19 - 21 (Table 7), these radicals were assigned the structures 95a - 95d, respectively.

Table 7. Hfsc's (G) of 95a - 95f in DMSO

95	a_{aromatic}^{H}	Other hfsc
a, X = C=O; Y = N^-	2.82, 1.91, 0.78, 0.35	$a^N = 0.78$
b, X = SO_2; Y = N^-	3.75, 2.70, 0.95, 0.75	$a^N = 0.35$
c, X = SO_2; Y = CH^-	3.96, 2.47, 1.00, 0.49	$a_{CH^-}^{H} = 1.47$
d, X = SO_2; Y = CD^-	3.96, 2.47, 1.00, 0.49	$a_{CD^-}^{D} = 0.22$
e, X = O; Y = CH_2	2.08, 2.08, 0.55, 0.55	$a_{CH_2}^{H} = 11.78$
f, X = S; Y = CH_2	2.00, 2.00, 0.63, 0.63	$a_{CH_2}^{H} = 7.25$

The postulated loss of a proton at the 3-position in 95a - 95c under the strongly basic conditions (potassium t-butoxide/DMSO) to give the radical dianion structure is based upon several observations. First, hfsc's for only four non-equivalent hydrogens (instead of the expected five) were observed for both 95a and 95b. By comparison to 83h, a hfsc would be expected for a hydrogen at that position if it were present. Secondly, the spectrum of 95c (Figure 21) clearly lacks 1:2:1 triplets which would be expected if a methylene group were present at the 3-position. Furthermore, only one hydrogen in 95c is exchanged in basic DMSO-d_6 as is evidenced by the spectrum of 95d. This strongly indicates the presence of only one hydrogen at the 3-position in 95c. Finally, 95a - 95c are heteroatom derivatives of 90 which is readily formed and is very stable.

Interestingly, an examination of several resonance structures for 90 and 95a - 95c indicates that the radical dianions can be considered as 10 π-electron systems in analogy to naphthalene and can therefore be considered as aromatic. Perhaps this aromatization accounts for their facile formation and high stability. The observed and calculated spin densities for 95a are given in Table 8.



95a

Table 8. Observed and calculated spin densities of 95a[a]

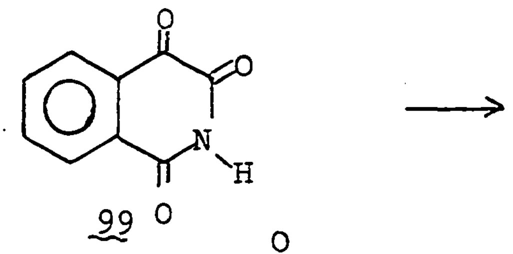
Position	Calculated		Observed
	Hückel	McLachlan	
1	0.2467	0.3250	
2	0.1787	0.2220	
3	0.0093	-0.0190	
4	0.0937	0.1140	

[a] $\beta_{C=O} = \beta_{C=N} 1.0\ \beta_{CC}$; $\alpha_O = \alpha_C + 1.8\ \beta_{CC}$; $\alpha_N = \alpha_C + 1.5\ \beta_{CC}$.

Table 8 (Continued)

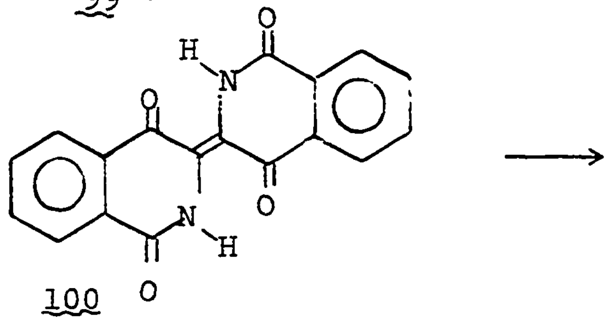
Position	Calculated Hückel	 McLachlan	Observed
5	0.0411	0.0177	0.033
6	0.0634	0.0553	0.081
7	0.0171	-0.0068	0.015
8	0.0837	0.0845	0.119
9	0.0023	-0.0395	
10	0.0375	0.0366	
11	0.1077	0.1071	
12	0.0780	0.0725	
13	0.0409	0.0318	

Good yields of 95a could also be obtained by reacting either phthalonimide, 99, or carbindigo, 100, with basic DMSO or basic methanolic solutions of hydrazobenzene. Interestingly, dissolution of N,N'-dimethylindigo, 101, into basic DMSO proved to be one of the best sources of the N-methylisatin radical anion, 83g. Monomethylindigo gave only the spectrum of 83g in the presence of oxygen while indigo itself failed to give an ESR spectrum of isatin radical anion. The formation of 95a from 100 presumably results from the reduction of 99 formed from the hydrolysis of 100 (Scheme VII). The presence of hydrazobenzene in the



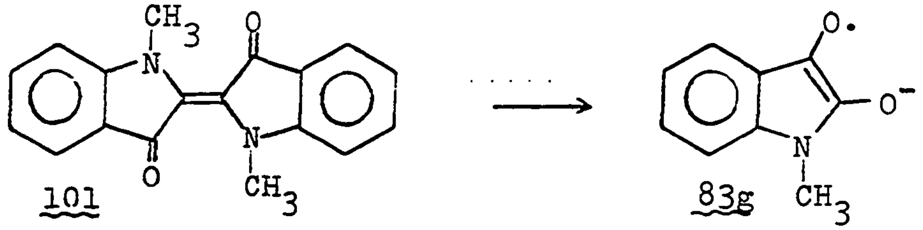
99

95a



100

95a

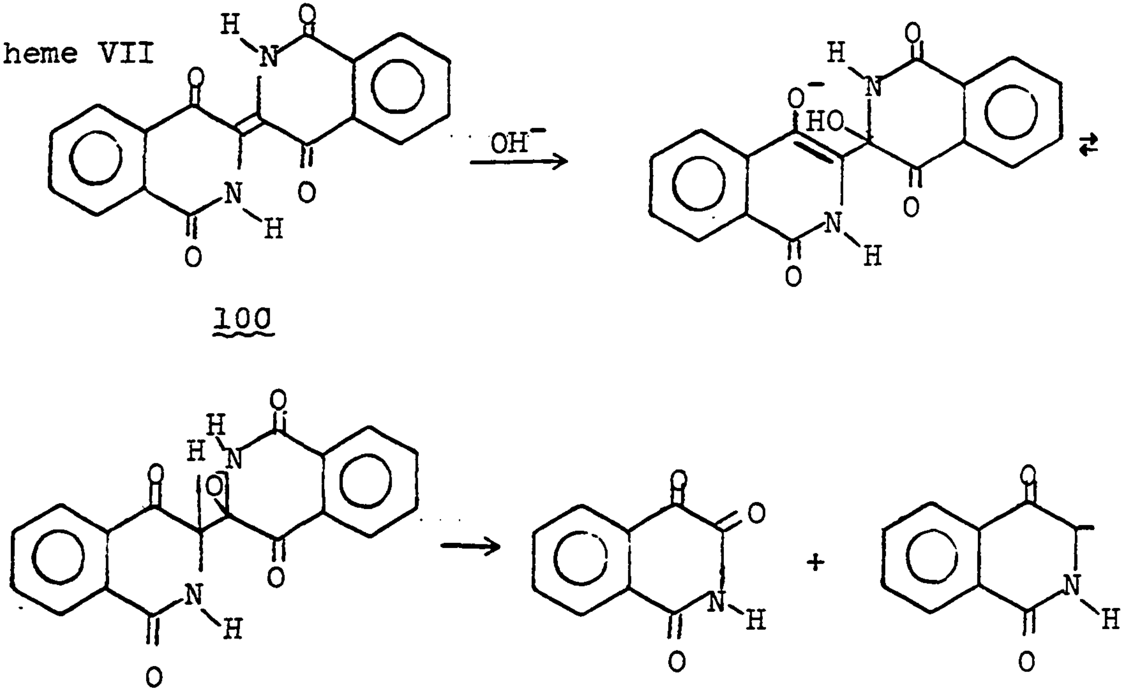


101

83g

methanolic solution is necessary for the reduction of 99.

Scheme VII

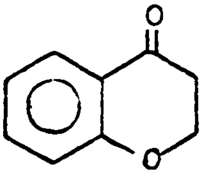


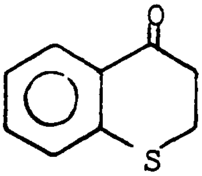
100

99

Although 96 - 98 could be readily converted into their corresponding semidiones, deprotonation also occurred giving radical dianions (95a - 95c) which could be considered aromatic. Since this aromatization was possibly a predominate factor in both the facile formation and the high stabilities of these radical dianions, it was necessary to examine heteroatom derivatives of α-tetralone in which aromatization would be unlikely to accompany semidione formation. Three such derivatives studied were 4-chromanone, 102, 4-thiochromanone, 103, and 4-tetrahydroquinolone, 104.

Exposure of basic DMSO solutions of 102 to oxygen produced a radical which gave the ESR spectrum shown in Figure 22. Although this radical slowly decayed, it could be regenerated by the addition of more air. The spectrum in Figure 22 consists of a triplet of triplets with a^H = 3.33 (2H) and 1.38 (2H) G. Interestingly, the hfsc's reported for o-semiquinone, 105, in aqueous solution are 3.65 (2H) and 0.95 (2H) G (53). Apparently 4-chromanone is oxidized to to o-semiquinone under these conditions. Similar treatment of 103 also produced a radical; however, no structure could be assigned.


102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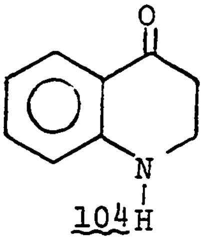
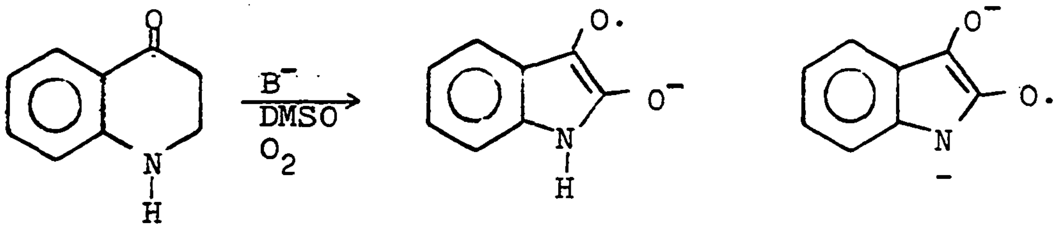

104

102

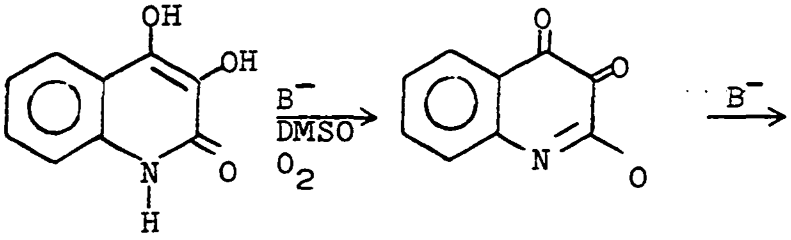
105

The addition of air to a solution of 104 in basic DMSO resulted in the formation the isatin radical anion, 83h. In some instances a mixture of radicals was obtained presumably



104 83h 83i

consisting of 83h and 83i. Previous work in these laboratories (54) has shown that the isatin radical anion is also produced from 2-oxo-3,4-dihydroxy-1,2-dihydroquinoline, 106, upon similar treatment possibly through the formation of the triketone anion intermediate 107. It is conceivable that 104



83h

106 107

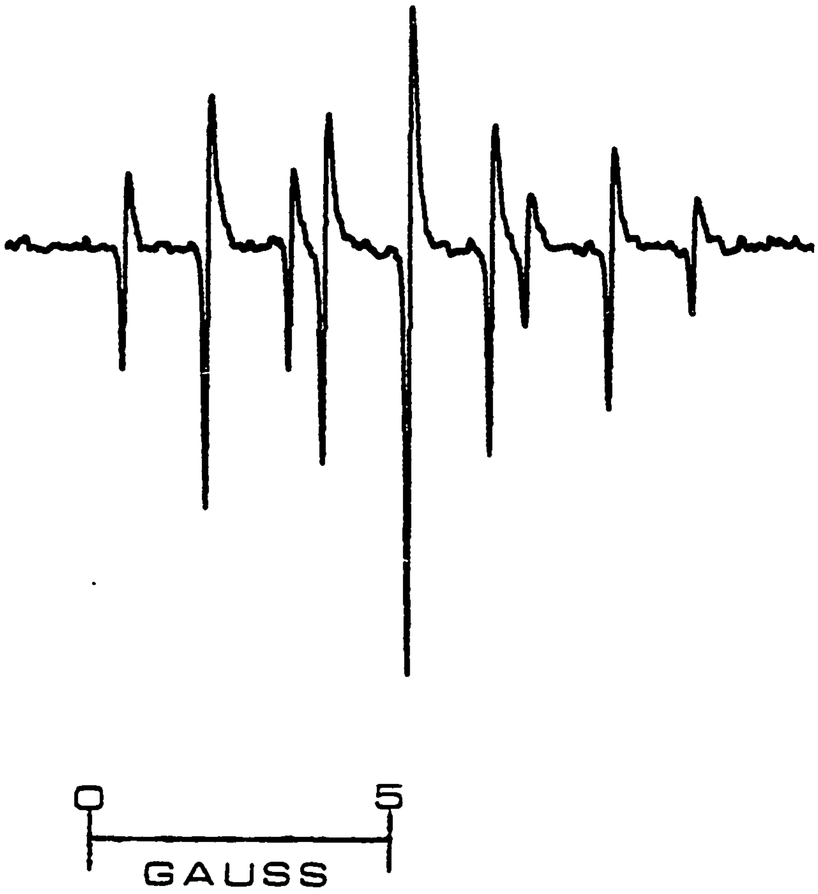
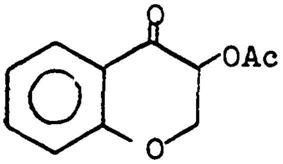
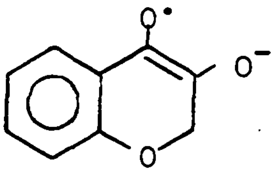


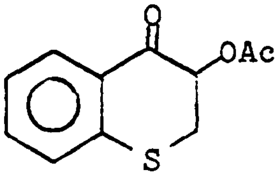
Figure 22. The first derivative ESR spectrum of o-semiquinone, 105, in DMSO

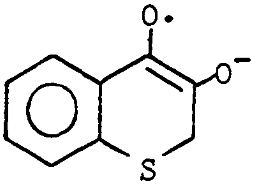
could be oxidized initially to form 107 which is then converted to 83h under the basic conditions.

Since 102 - 104 could not be converted to the semidiones with structure 95 by treatment with oxygen in basic DMSO, the acetoxy derivatives, 108a and 108b, were prepared from 102 and 103, respectively, by their reaction with lead tetraacetate. The reaction of 108a and 108b with either basic methanolic solutions of azobenzene or approximately one equivalent of potassium t-butoxide in DMSO did give rise to the formation of 95e and 95f, respectively. However, the ESR spectra obtained from 95e (Figure 23) and 95f (Figure 24) indicated that the radicals were formed in very low concentration followed by a slow decay. The large difference in the methylene hfsc's (Table 7) for 95e (11.78 G) and 95f (7.25 G) is unexpected.


108a


95e


108b


95f

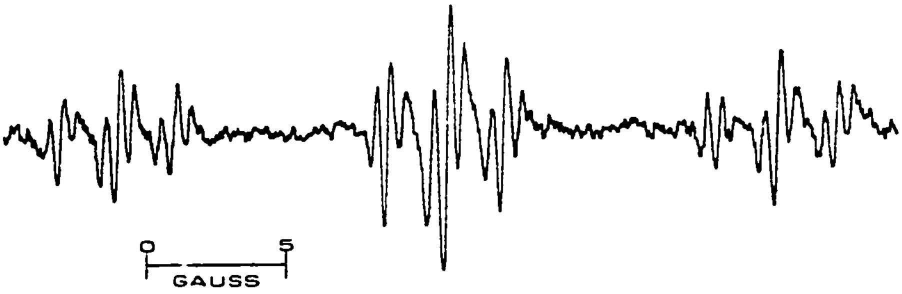


Figure 23. The first derivative ESR spectrum of 95e in DMSO

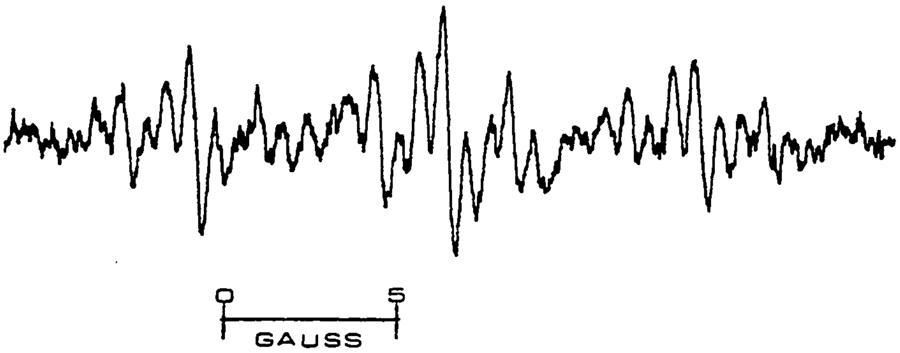
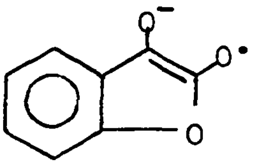
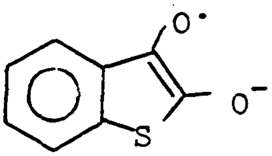


Figure 24. The first derivative ESR spectrum of **95f** in DMSO

The reaction of 108a and 108b with DMSO solutions containing an excess of potassium t-butoxide in the absence of oxygen gave ESR spectra consisting of 1:3:3:1 quartets of 6.7 - 6.8 G. No attempts were made to assign structures to these radicals. Exposure of these solutions to oxygen resulted in the formation of 83e and 83f, respectively. It would seem reasonable by analogy to 104 that 108a and 108b



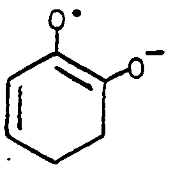
83e



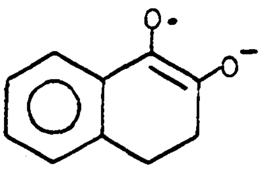
83f

are oxidized to derivatives of the triketone anion, 107, which are converted under the basic conditions to 83e and 83f.

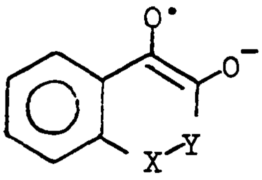
Several observations concerning the preparation of 88 and 95 deserve mention. The stabilization obtained by substituting a double bond with a benzo group also exists for unsaturated semidiones in the six-membered ring. In contrast to 53 which could not be observed under flow conditions, 88 could be observed statically and decayed only slowly at room temperature in DMSO.



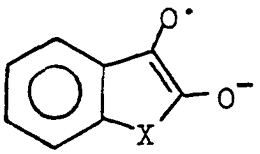
53



88



95



83

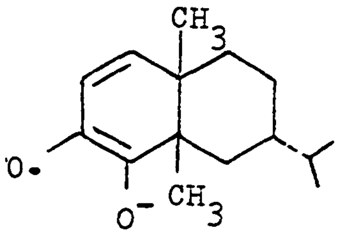
Both **95e** and **95f** parallel **88** in that they are formed in low yields and decay slowly in DMSO solution at room temperature. This seems to substantiate an earlier suggestion that the high stabilities of **95a** - **95c** reflect the fact that these radical dianions are aromatic. Interestingly, the semidiones formed from the oxidation of **104**, **108a**, and **108b**, (**83h**, **83e**, and **83f**) are also aromatic.

Finally, the results of the HMO calculations of **95a** show that the positions of high spin density in the aromatic rings in both **95** and **83** are analogous. In addition, an examination of Tables 6 and 7 reveals that the magnitudes of the hfsc's in the aromatic rings of **95** and **83** are also similar.

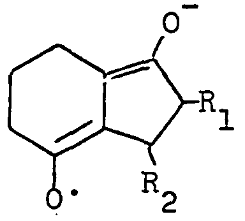
UNSATURATED SEMIDIONES DERIVED FROM FUSED CYCLOHEXANE RING SYSTEMS

Only a few examples of conjugated unsaturated semidiones in bicyclic and polycyclic ring systems (Chart II) have been reported (7, 34). In some instances assignments of both structure and hfsc's for these radicals were only postulated since a systematic study of unsaturated semidiones in cyclic systems had not been undertaken.

Chart II

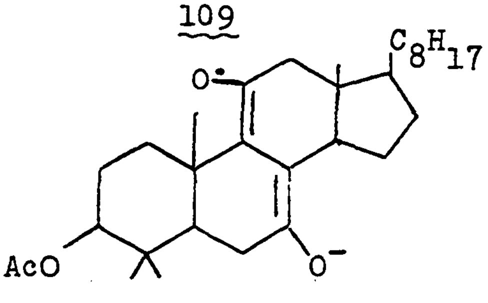


109



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

110



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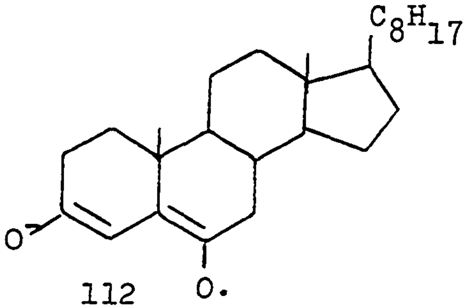

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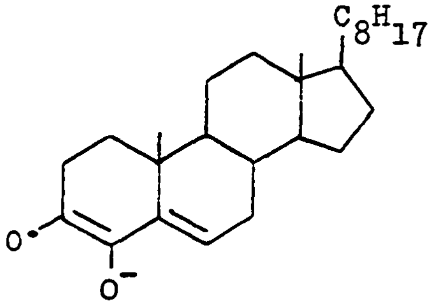

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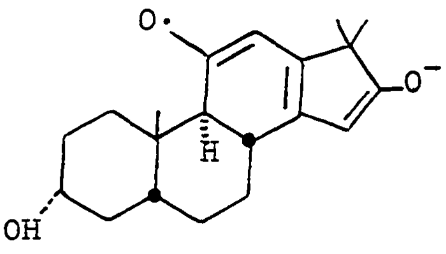

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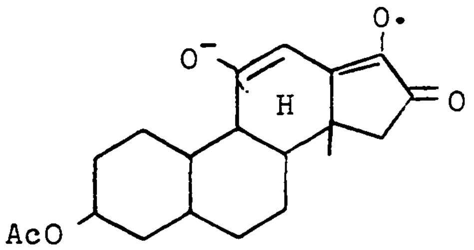

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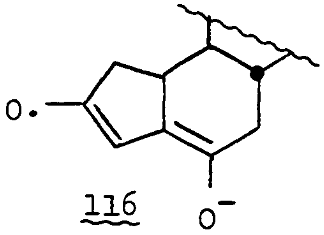

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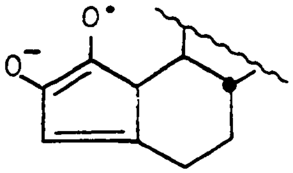
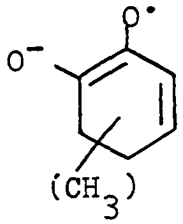


117

As a continuation of our studies on unsaturated semidiones in cyclic systems, our attention was next focused on unsaturated semidiones derived from the octalin ring system. It was hoped that these studies could be utilized not only as a basis for a reconsideration of 109 - 117, but also as a basis for future work concerned with solving structural and conformational problems.

In view of the work on unsaturated semidiones in the five- and six-membered rings, comments on structures 109 and 117 are in order. The ESR spectrum of 109 gave hfsc's of 5.45 (1H) and 1.75 (1H) G which were assigned to the α- and β-positions, respectively. The hfsc's observed for the α- and β-positions in the structurally similar semidiones, 49, were experimentally found to be 1.5 - 1.75 and 4.8 - 5.5 G, respectively. This clearly indicates that the original assignments in 109 should be reversed; which also, incidentally, results in excellent agreement between the two systems.



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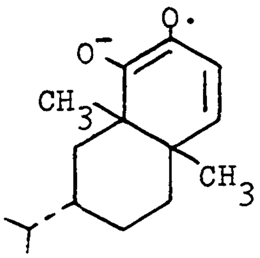
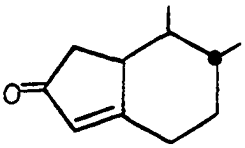
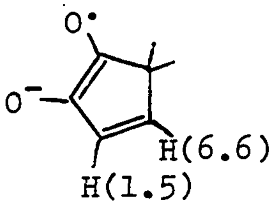


109

The oxidation of A-norcholest-3-en-2-one, 118, resulted in the formation of two radicals which were postulated to have structures 116 and 117. The ESR spectrum presumably due to 117 gave hfsc's of 6.98 (1H) and 1.07 (1H) G (7). On the basis of the assigned hfsc's in 46, it is possible



118



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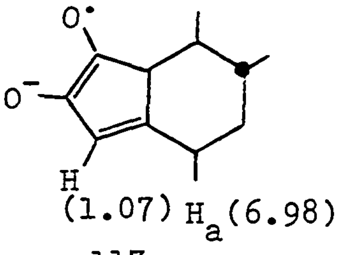
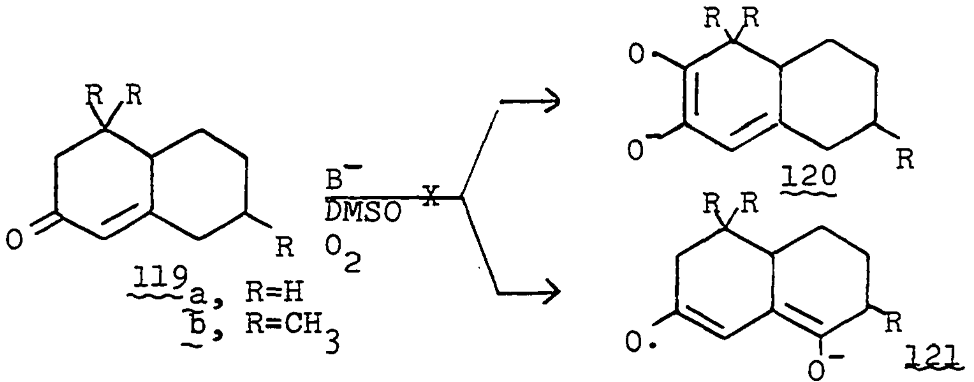


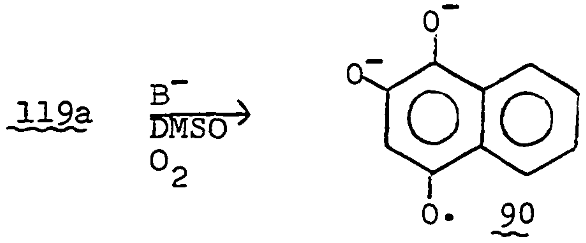
117

that the 1.07 G splitting arises from the vinyl hydrogen while the 6.98 G splitting comes from the axial hydrogen at C-6. The lack of hfsc's from the equatorial hydrogen at C-6 and the axial hydrogen at C-10 does seem unlikely.

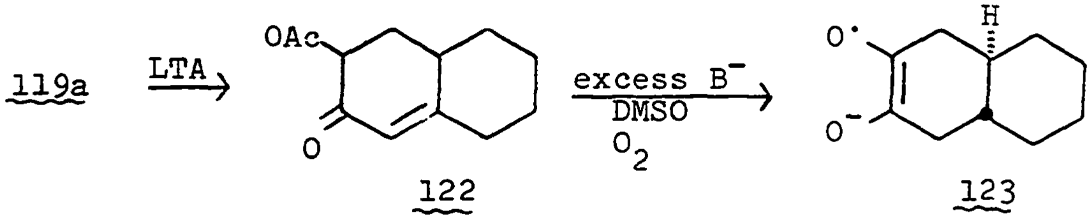
Oxidation of either $\Delta^{1,9}$-2-octalone, 119a, or its 4,4,7-trimethyl derivative, 119b, in basic DMSO solution failed to give either their $\Delta^{1,9}$-2,3-semidiones (120a and 120b, respectively) or $\Delta^{1,9}$-2,8-semidiones (121a and 121b, respectively). Surprisingly, the addition of large amounts



of oxygen to a solution of 119a in basic DMSO gave an ESR spectrum of the radical dianion 90.

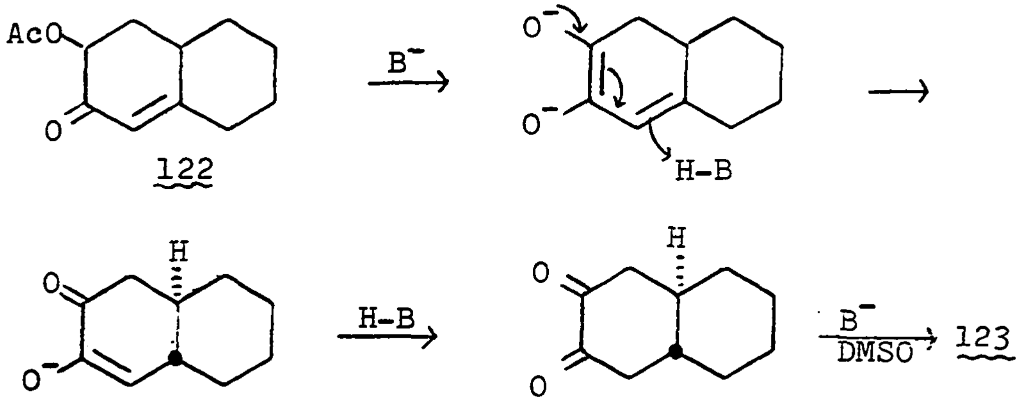


In an attempt to prepare 120a, 119a was reacted with lead tetraacetate (LTA) to give 122 in an isolated yield of 35%. The reaction of 122 with basic DMSO either statically or under flow conditions failed to give the semidione 120a. Moreover, when a DMSO solution of 122 containing an excess of potassium t-butoxide was exposed to



oxygen, an ESR spectrum (Figure 25) of the saturated semidione 123 (3) was recorded. The addition of more oxygen destroyed 123 and produced 90. Since the spectrum in Figure 25 indicates the presence of the semidione with the *trans* ring fusion only, protonation of the dianion (Scheme VIII) is presumably occurring exclusively *trans* to the C-10 hydrogen.

Scheme VIII



In a final attempt to prepare a $\Delta^{1,9}$-2,3-semidione, $\Delta^{1,9}$-10-methyl-2-octalone was reacted with lead tetraacetate to give a *cis* and *trans* mixture (3:2 ratio of isomers) of $\Delta^{1,9}$-3-acetoxy-10-methyl-2-octalone, 124, in a combined and isolated yield of 34%. The reaction of 124 with basic DMSO under flow conditions produced a radical which gave the spectrum in Figure 26. On the basis of the hfsc's (a^H = 11.20 (1H), 8.56 (1H), 2.04 (1H), 1.36 (1H), and 0.88 (1H) G) obtained from this spectrum, the radical was assigned the structure of the $\Delta^{1,9}$-2,3-semidione, 125. An examination of

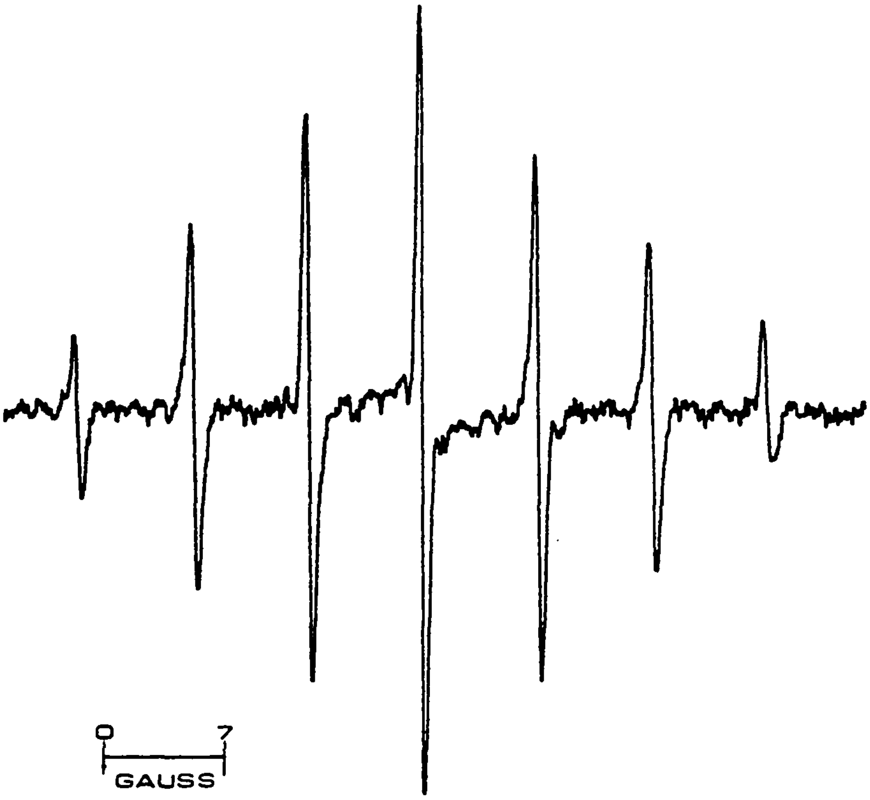
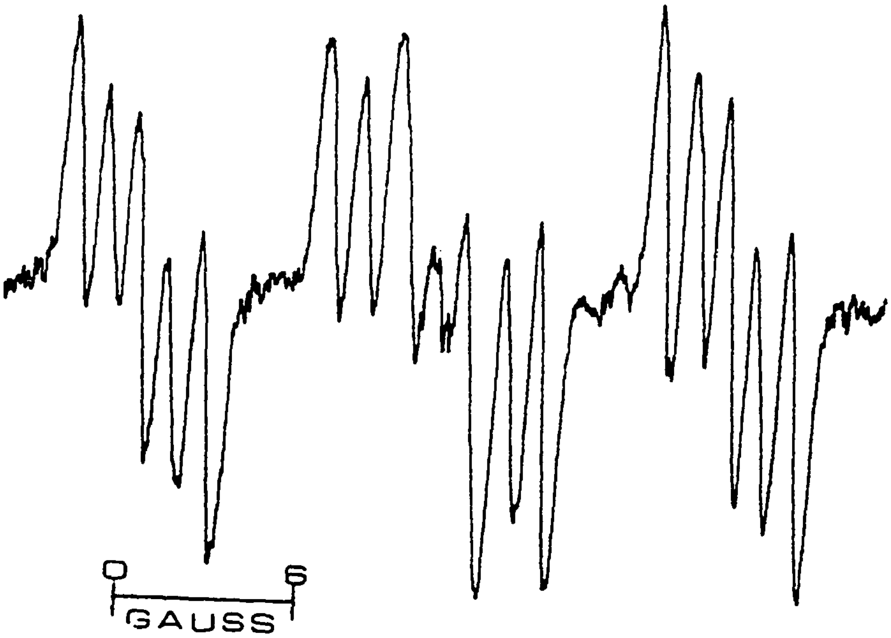


Figure 25. The first derivative ESR spectrum of trans-decalin-2,3-semidione in DMSO

Figure 26. The first derivative ESR spectrum of $\Delta^{1,9}$-10-methyl-octalin-2,3-semidione, 125, (top) in DMSO; calculated spectrum (bottom) with Lorentzian linewidth 1.12 gauss and splitting constants from text performed by JEOLCO-JNM-RA-1 spectrum accumulator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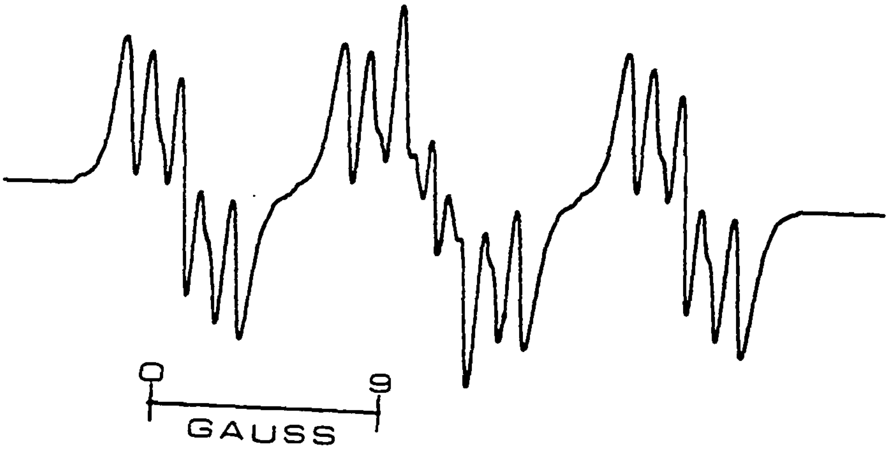
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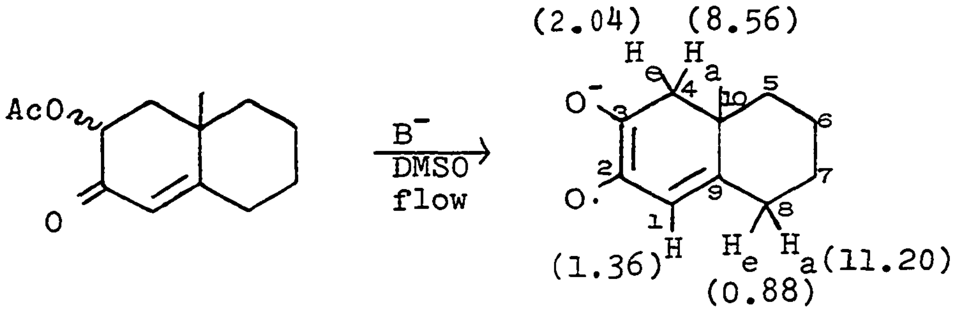


125

a Dreiding Model of 125 reveals that the axial hydrogen at C-8 has a smaller dihedral angle than the quasi-axial hydrogen at C-4. Therefore, the large 11.20 and 8.56 G couplings were assigned to the axial C-8 and quasi-axial C-4 hydrogens, respectively. The 1.36 G coupling was assigned to the vinyl hydrogen based on the results obtained for 49. Finally, since the spin densities at the C-4 and C-8 positions are possibly similar in magnitude (by comparison to 49), the 2.04 and 0.88 G couplings were assigned to the quasi-equatorial and equatorial hydrogens at these positions, respectively.

Interestingly, in contrast to 122 which gave only the trans ring fusion saturated semidione upon treatment with basic DMSO and oxygen, 124 reacted with excess potassium t-butoxide in DMSO in the absence of oxygen to give an ESR spectrum (Figure 27) of both the cis and trans ring fusion saturated semidiones. The ratio of the cis:trans isomers appeared to vary with the concentrations of both the base and the acetoxy ketone.

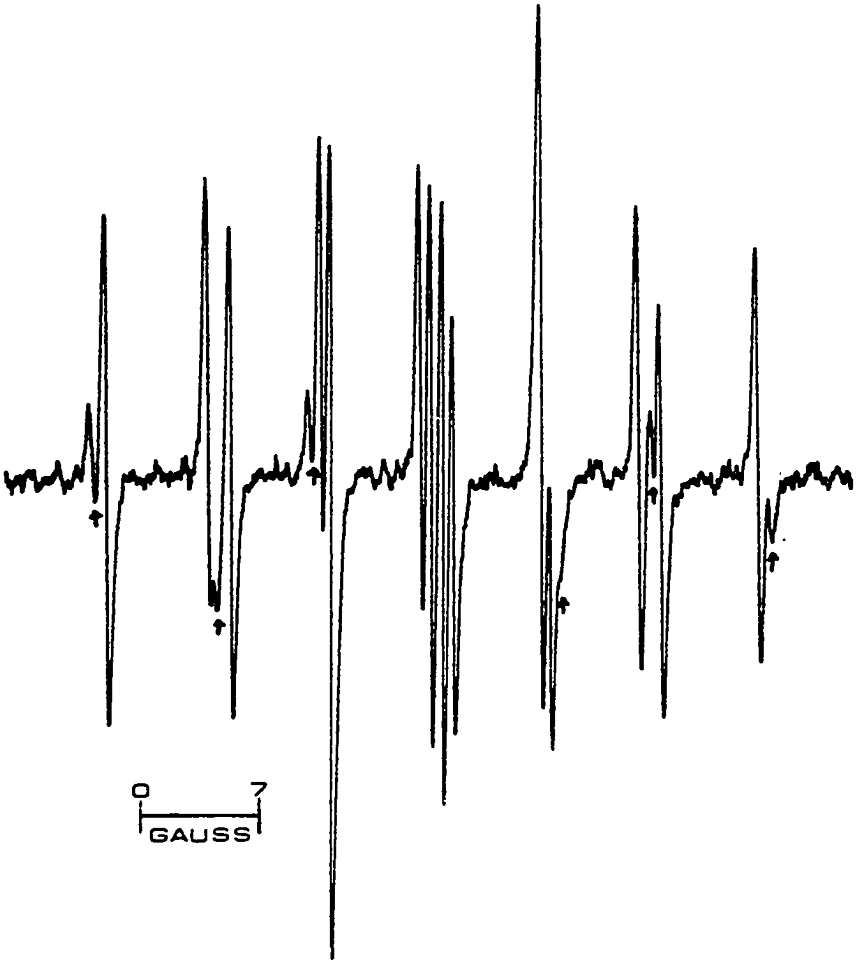
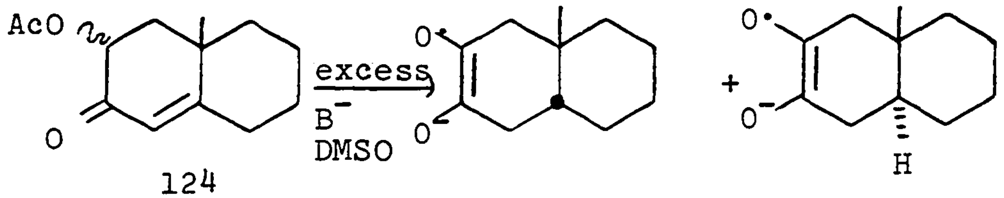
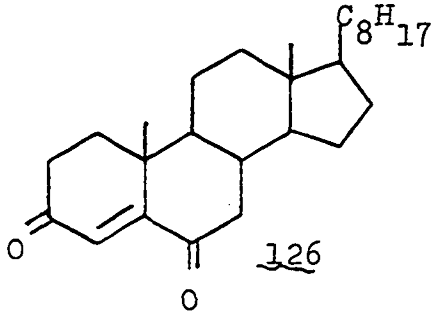


Figure 27. The first derivative ESR spectrum of trans-10-methyldecalin-2,3-semidione and a trace of cis-10-methyldecalin-2,3-semidione (designated by arrows) in DMSO



124

Samples of both 126 and 127 were received as gifts from Dr. Malhotra (55). The reaction of 126 with basic DMSO under static conditions gave as before (7) a poorly resolved ESR spectrum (Figure 28) which gave approximate values of a^H = 9.3 (1H), 5.4 (2H), 2.5 (1H), and 1.6 (1H) G. Presumably, the radical under observation has the structure of the radical anion 112.



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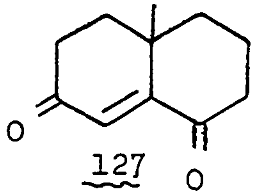


127

The reaction of 127 with basic DMSO gave the complex ESR spectrum shown in Figure 29. This spectrum was also obtained when $\Delta^{1,9}$-10-methyl-2-octalone was oxidized in basic DMSO. Although a complete analysis of the spectrum was not obtained, the total width of the spectrum (25.75 G) is similar to that of 112 (24.20 G) which suggests that the structure of the radical is 128.

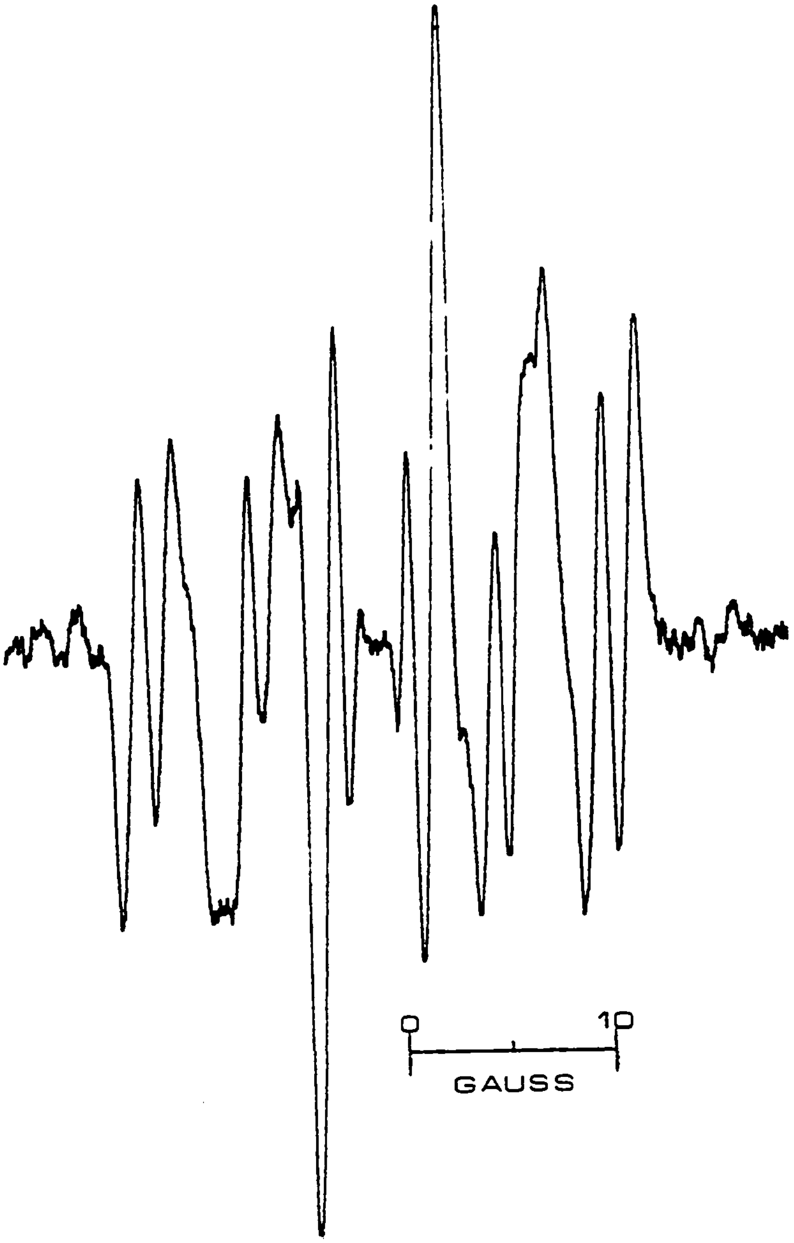


Figure 28. The first derivative ESR spectrum of 112 in DMSO

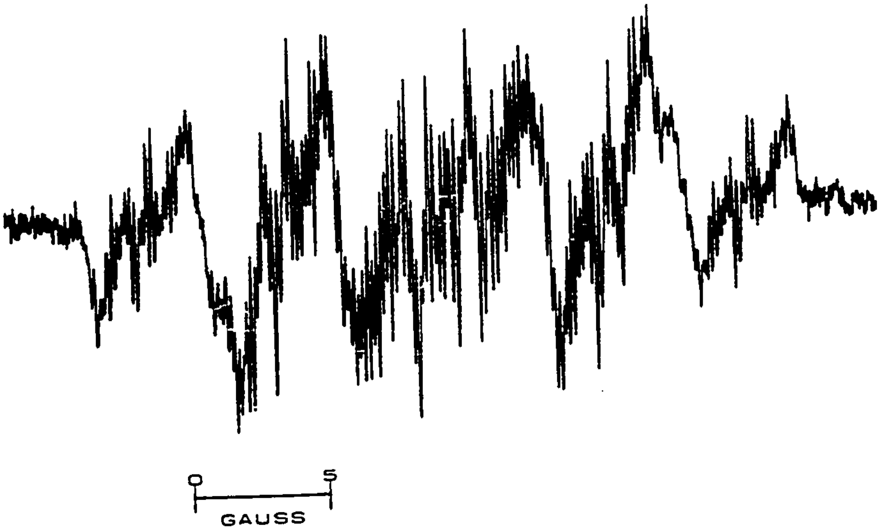
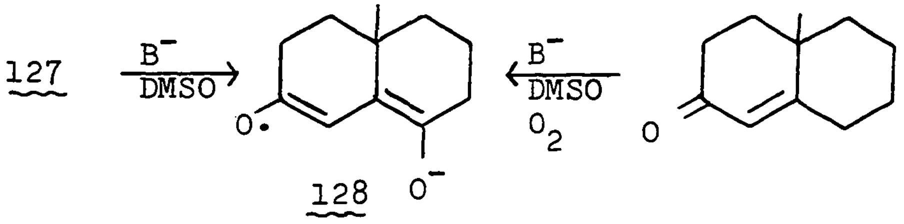
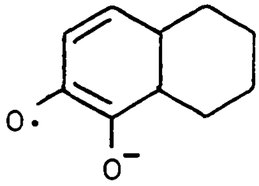


Figure 29. The first derivative ESR spectrum of 128 in DMSO



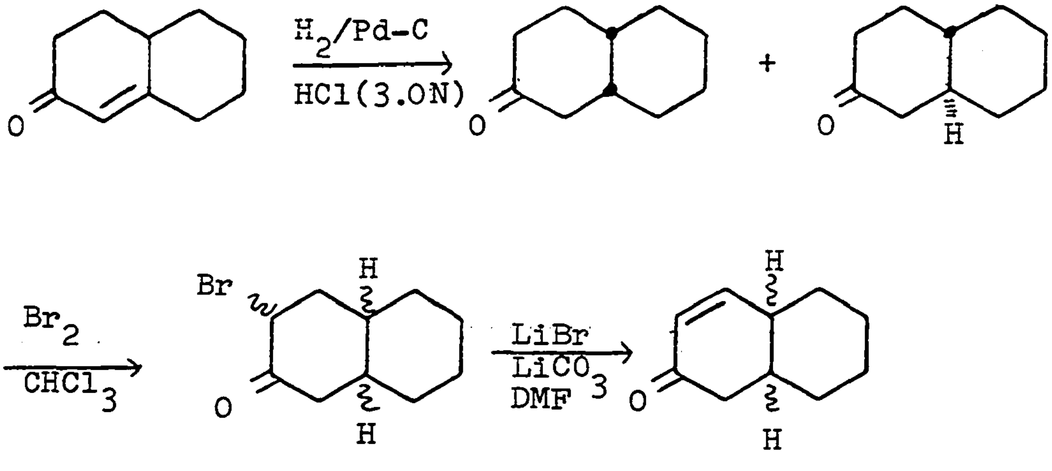
128

In an attempt to prepare the $\Delta^{3,4}$-1,2-semidione, 129, which has a structure analogous to 109, $\Delta^{1,2}$-3-octalone, 130, was prepared from $\Delta^{1,9}$-2-octalone (Scheme IX). The hydro-



129

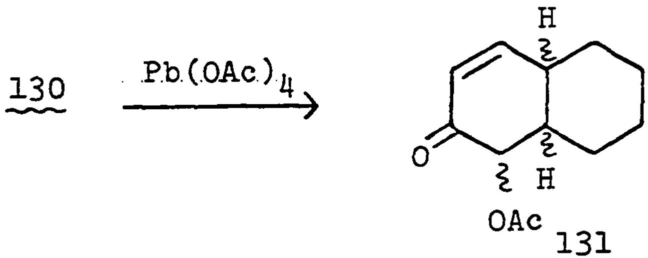
Scheme IX



130

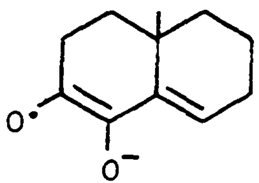
genation was carried out under reaction conditions which were reported to give a 9:1 ratio of the *cis*:*trans* ring fusion decalones (56). Although no attempts were made to confirm this report, the mixture of 130 obtained contained predominately one isomer.

The reaction of 130 with lead tetraacetate resulted in the formation of at least four acetoxy ketones. One of these acetoxy ketones, 131, was isolated in crystalline form. No attempts were made to separate the remaining products. No ESR signal was observed when 131 (one isomer) was reacted with basic DMSO under static conditions. Since only a small amount of 131 was available, its reaction with basic DMSO under flow conditions could not be carried out.



131

In an attempt to prepare the $\Delta^{8,9}$-1,2-semidione 132, $\Delta^{8,9}$-10-methyl-1-octalone, 133, was synthesized according



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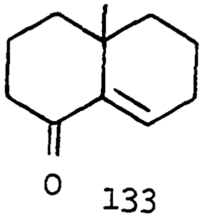
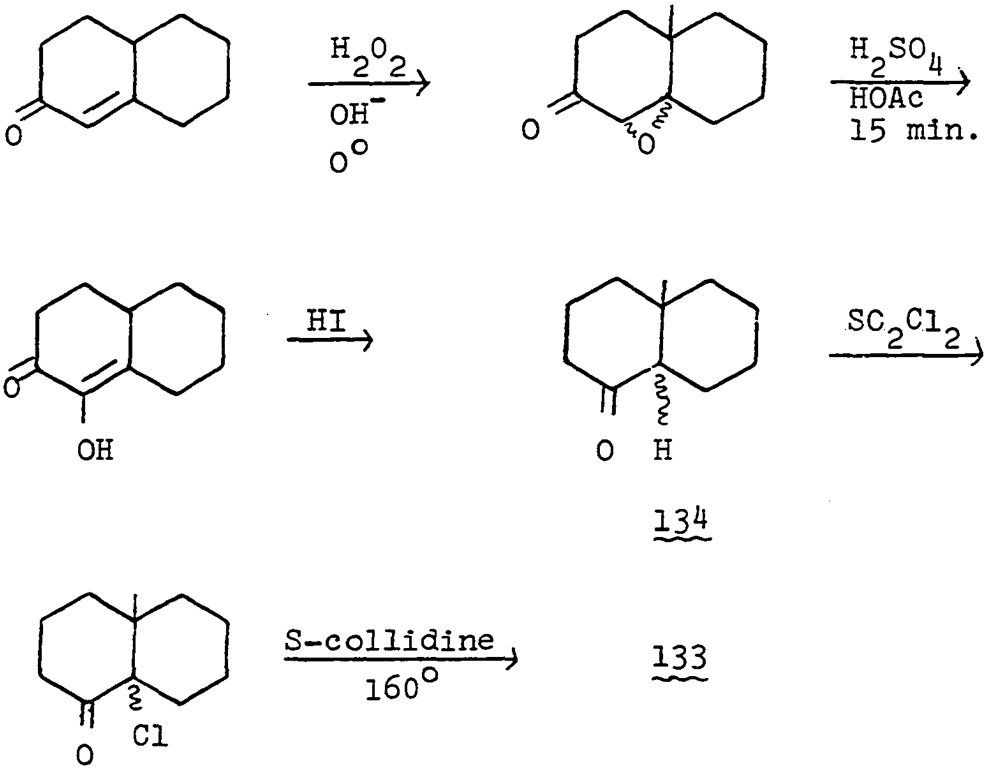


133

to the procedure outlined in Scheme X. Although the reaction sequence leading to the formation of the decalones, 134, was originated by House *et al.* (57) for the synthesis of a derivative of 134, some of the experimental conditions were altered.[5] The remaining part of the sequence was originated by Scanio and Mosbey. The overall yield of 133 was about

Scheme X



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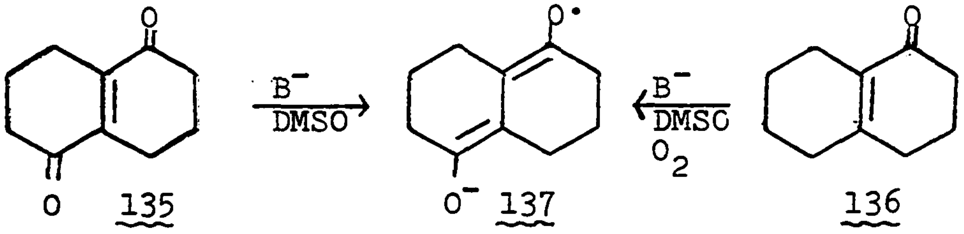
[5] C. Scanio and D. Mosbey, unpublished results, Iowa State University, Ames, Iowa. Private communication, 1971.

35 - 40% which reflects the low yield of the diketone obtained from the acid catalyzed rearrangement of the epoxides. A small amount of the $\Delta^{2,3}$-isomer was obtained in addition to 133 presumably originating in the chlorination step where a small amount of the 2-Cl derivative is formed.

Oxidation of 133 in basic DMSO solution failed to generate a radical. The reaction of 133 with lead tetraacetate resulted in a product mixture which gave no NMR absorption in the olefinic region. No attempt was made to characterize these products. The enone chromophore in 133 has also been observed by Scanio and Mosbey to be quite labile.

The reaction of $\Delta^{9,10}$-octalin-1,5-dione, 135, with potassium t-butoxide in DMSO at room temperature produced a radical which gave a poorly resolved ESR spectrum (Figure 30) consisting of a nine line multiplet. Exposure of this solution to oxygen resulted in an increase in resolution as evidenced by the ESR spectrum in Figure 31. The spectrum in Figure 31 was also obtained by oxidizing basic DMSO solutions of $\Delta^{9,10}$-1-octalone, 136. Overmodulation of the spectrum in Figure 31 produced the spectrum in Figure 30. These facts indicated that the same radical was under observation in both spectra. The radical was assigned the structure 137.



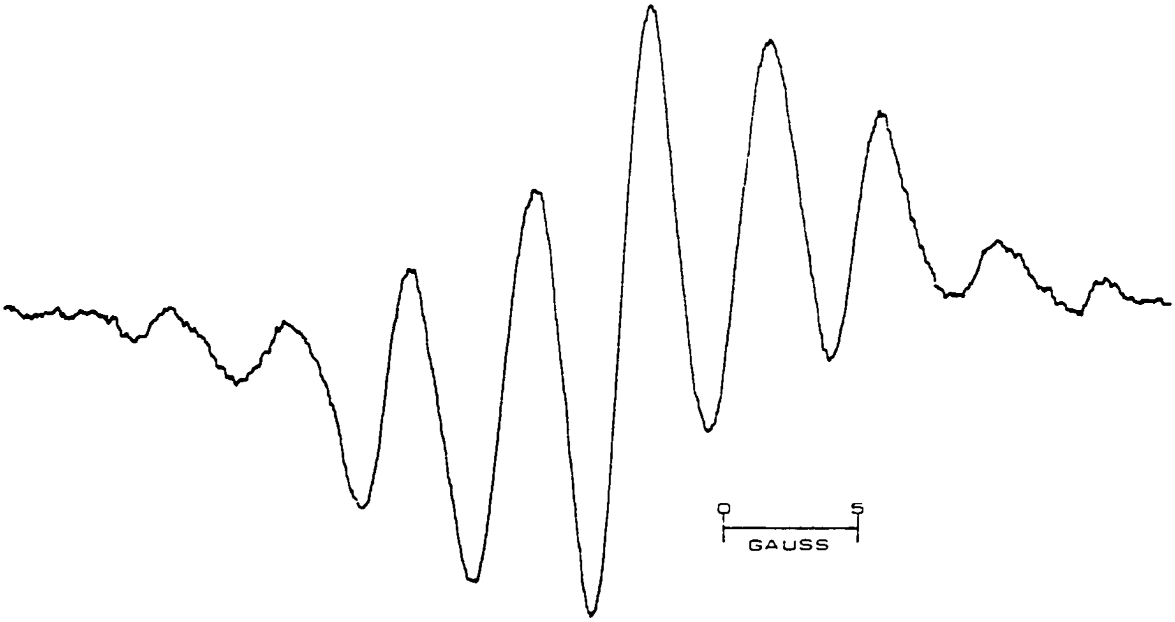


Figure 30. The first derivative ESR spectrum of $\Delta^{9,10}$-octalin-1,5-semidione, 137, generated from 135 with basic DMSO

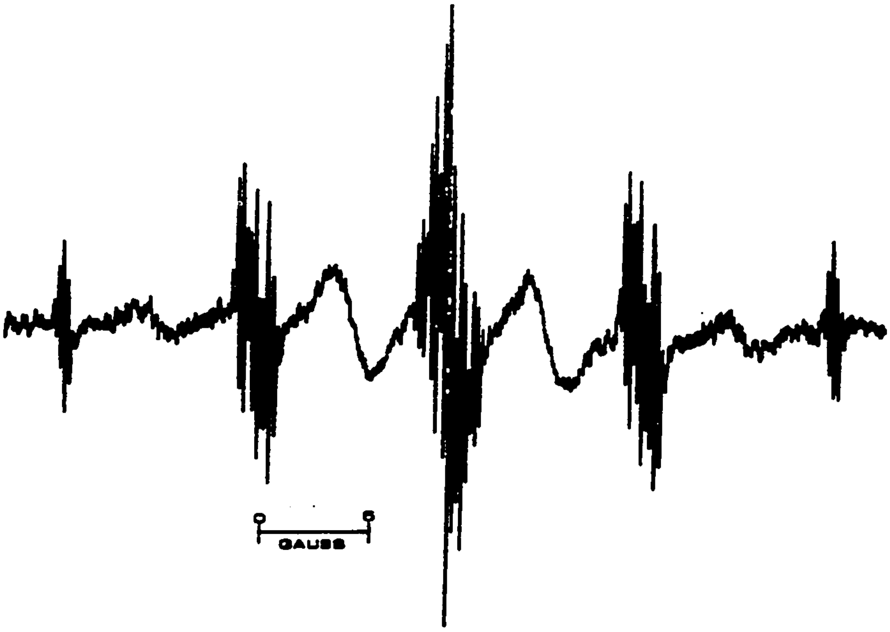
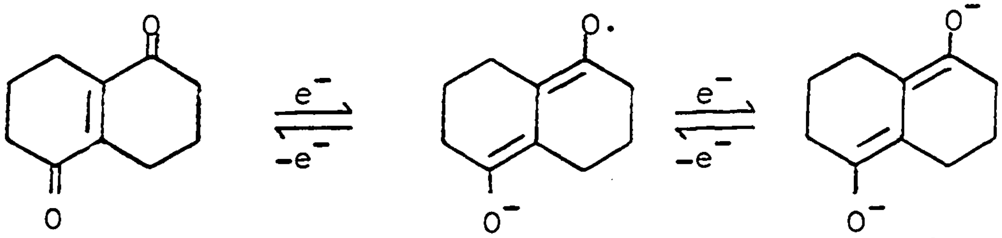


Figure 31. The first derivative ESR spectrum of $\Delta^{9,10}$-octalin-1,5-semidione, 137, generated from 136 upon oxidation in basic DMSO

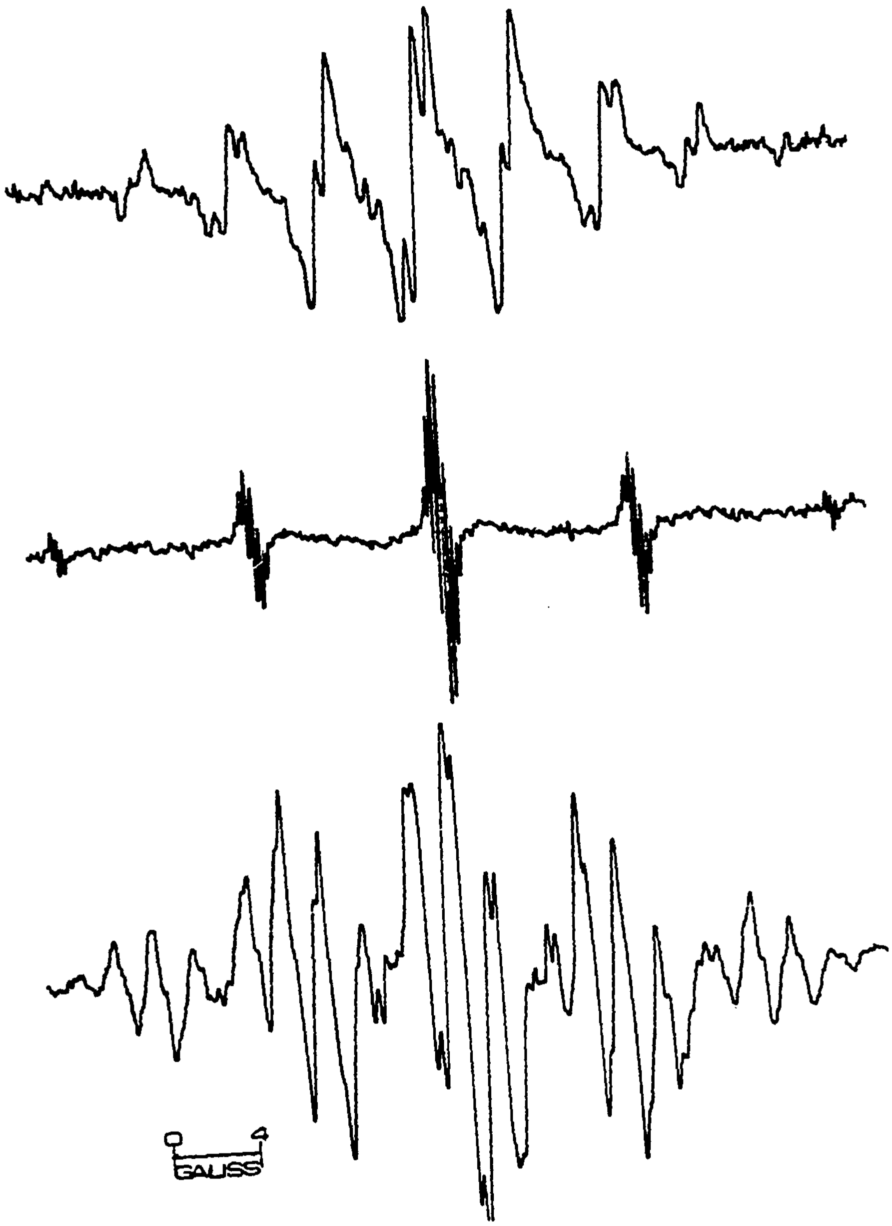
Two types of line broadening are occurring in the spectra of Figures 30 and 31. In the spectrum of Figure 30 all of the lines are broadened while in Figure 31 only the alternate lines are affected. In general the width of a line increases with decreasing lifetime of the radical under observation. The broadening in Figure 30 presumably results from the fact that the lifetime of the spin states of 137 when generated from 135 in DMSO solution is very short. This short lifetime could arise from a rapid electron transfer reaction between 137 and either 135 or its dianion 138. The addition of oxygen disrupts the electron transfer reaction and increases the lifetime of the spin states of 137 resulting in the observation of better resolution (Figure 31).



135 137 138

The broadening observed in Figure 31 where only alternate lines are affected is called linewidth alternation (for an excellent discussion of linewidth alternation see Reference 58). This broadening is strongly temperature dependent as evidenced by the ESR spectrum of 137 (Figure 32) generated from 136 in 80% DMSO/20% t-BuOH at 0°. The

Figure 32. The first derivative ESR spectrum of $\Delta^{9,10}$-octalin-1,5-semidione, 137, in DMSO at 105° (top), in 80% DMSO/20% *t*-BuOH at 0° (middle) and in DMF at -50° (bottom)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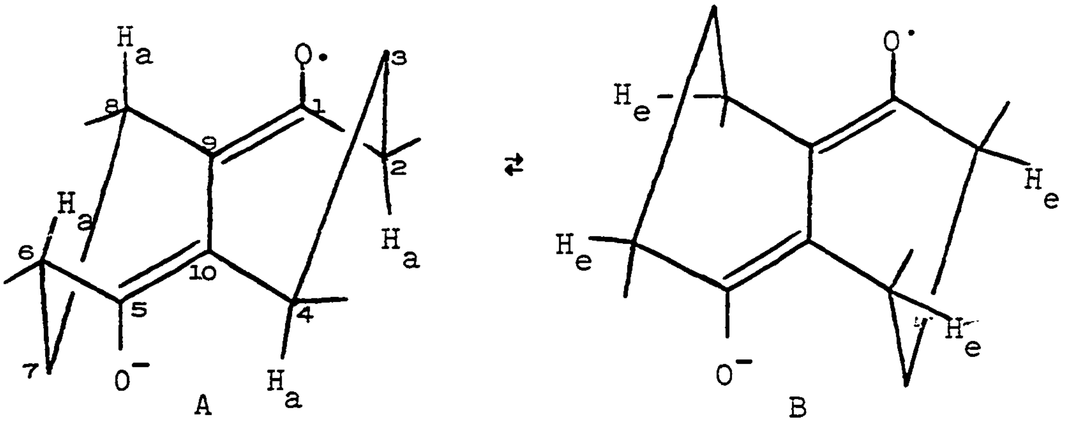
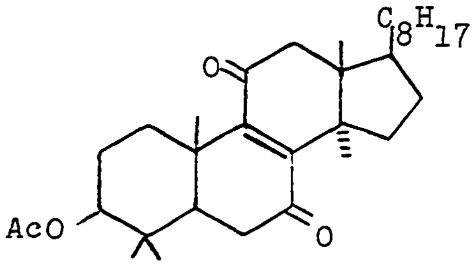
broadening in this spectrum is so severe that the alternate lines are almost no longer observable. The linewidth alternation affect for 137 presumably arises from a slow interconversion between conformers A and B at temperatures close to 0-25°. This is substantiated by an examination of the spectra obtained for 137 at 105° (generated from 136 in basic DMSO solution) and -50° (generated electrolytically in DMF from 135) shown in Figure 32.



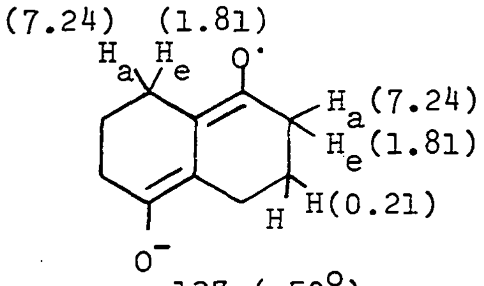
The spectrum of 137 at 105° consists of a nine line multiplet (with some additional splitting) with $a^H = 4.27$ (8H) G while the spectrum at -50° consists of a 1:4:6:4:1 quintet of quintets (with some additional splitting) with $a^H = 1.81$ (4H) and 7.24 (4H) G. In confomer A the designated hydrogens are quasi-axial and should have a large coupling constant while these same hydrogens in B are quasi-equatorial and should have a small coupling constant. At 105° these confomers are rapidly interconverting so that only an average coupling constant of the quasi-axial and quasi-equatorial hydrogens is observed at C-2, C-4, C-6 and C-8. Since nearly eight equivalent hydrogens are observed, the spin density at C-2 and C-6 must be comparable to the spin density at C-4 and C-8. At -50° the interconversion between A and B is sufficiently slow so that coupling constants of the quasi-axial (7.24 G) and quasi-equatorial (1.81 G) hydrogens are observed.

Thus far the hfsc's of the C-3 and C-7 hydrogens have been ignored. The outer lines in Figure 31 are 1:4:6:4:1 quintets with a splitting of 0.21 G which arise from the four equivalent hydrogens at these positions. Due to the small magnitude of the hfsc, these hydrogens do not give line-width alternation at these temperatures (0°-25°). The lifetime of confomers A and B is given by 1/k where k is the coalesence rate with the relationship, $k = 6.22 \times 10^6 (a_{ax}^H - a_{eq}^H)$. Below this exchange rate different magnetic environments for the quasi-axial and quasi-equatorial hydrogens exist giving rise to the observation of a_{ax}^H and a_{eq}^H (59). Therefore, confomers A and B have a lifetime of at least 3×10^{-8} sec at 0-25°.

Treatment of 139, or its saturated derivative, with basic DMSO yielded 111 with $a^H = 5.44$ (1H), 4.72 (1H), and 1.38 (2H) G (7). Since 139 is a rigid system, these hfsc's are in poor agreement with those observed for 137 at -50°. On the basis of 137 (-50°), two large splittings (7-8 G) for the quasi-axial hydrogens and two small splittings (2 G) for the quasi-equatorial hydrogens would be expected.

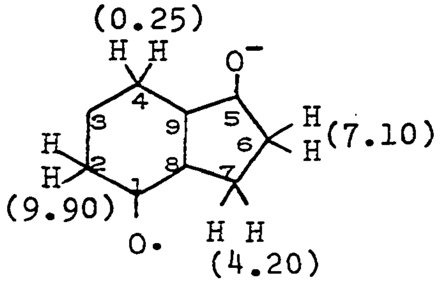


139



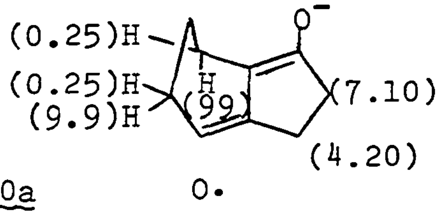
137 (-50°)

The original assignments of hfsc's at C-6 and C-7 in 110a were confirmed by methyl-substitution [34] and are consistent with 137. However, one of the 0.25 G and 9.90 G splittings at C-2 and C-4, respectively, should be interchanged by comparison to 137 (-50°). This implies that



original assignment

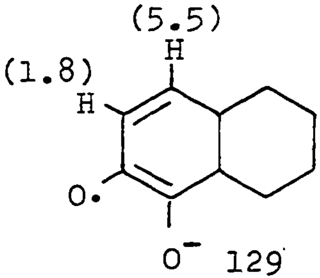
110a



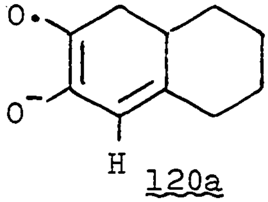
reassignment

the conformational interconversions in 110a are sufficiently slow (at room temperature) to allow observation of hfsc's for the quasi-axial and quasi-equatorial hydrogens.

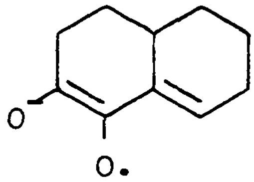
Of the four conjugated unsaturated 1,2-semidiones in the octalin ring system, examples of 120a and 129 are now known (with alkyl-substitution). There is a great tendency for

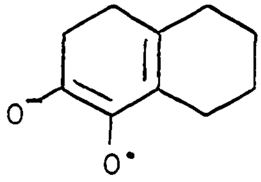


129



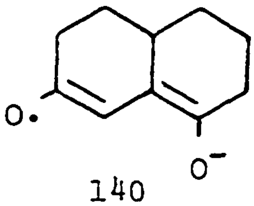
120a



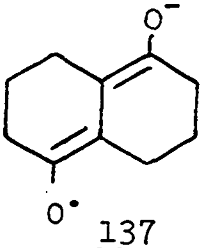


120a to yield saturated semidiones in basic DMSO solution. Unsaturated semidiones with structures similar to these four semidiones will probably not be useful in structural assignments by ESR spectroscopy because of their low stability and difficult synthesis.

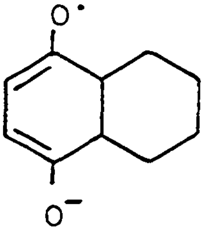
Of the three possible unsaturated 1,4-semidiones in the octalin ring system, examples of both 140 (with alkyl-substitution) and 137 have been provided in this work. The 1,4-semidiones are more stable than the unsaturated 1,2-semidiones and should be obtainable from proper precursors.



140



137



It was possible to study the conformational instability of **137** with ESR spectroscopy as a function of temperature.

EXPERIMENTAL

Reagents

Dimethyl sulfoxide was distilled from CaH_2 at reduced pressure and stored over molecular sieves. Potassium t-butoxide was obtained commercially and was used directly without further purification.

Preparation of Semidiones and Ketyls

The semidiones observed under static conditions were prepared as solutions in the standard apparatus (60). These radicals were generated from monoketones and hydroxy ketones in DMSO solution by methods previously described (34, 60). The semidiones and ketyls observed under flow conditions were generated by reacting deoxygenated DMSO solutions (250-500 mls) of acetoxy ketones and ketones (0.025 - 0.05 M) with deoxygenated solutions (250-500 mls) of potassium t-butoxide in DMSO (0.05 - 0.10 M) in the flow apparatus shown in Figure 1.

Recording of ESR Spectra

The ESR spectra were recorded from either a Varian E-3 spectrometer (4 inch magnet and 100 KHz field modulation) or a Varian V-4500 spectrometer (9 inch magnet and 100 KHz field modulation).

Characterization of Compounds

NMR spectra were recorded from either a Varian A-60 spectrometer or a Hitachi Perkin-Elmer R-20B spectrometer. Infrared spectra were recorded on a Perkin-Elmer Model 21 Double Beam Spectrometer. Mass spectra were recorded on either an Atlas CH4 spectrometer or an AEI-MS-902 spectrometer. All of the elemental analyses were made by Galbraith Laboratories, Inc.

Preparation of Compounds

General procedure for preparing acetoxy ketones

A mixture of the ketone, 1.1 equivalents of lead tetraacetate (61), and dry benzene (100 mls/0.05 moles of ketone) was heated to reflux for 2-3 days as described by Ellis (38). After cooling, the benzene solution was washed with water, sat. $NaHCO_3$, and sat. NaCl and was dried ($MgSO_4$). Removal of the benzene at reduced pressure left a liquid or solid which frequently consisted of acetoxy ketone and unreacted ketone. In general, separation of these compounds was possible.

Diphenylcyclopropenone

This compound was prepared according to the method of Breslow *et al*. (62): mp 119-120° [lit. (62) mp 119-120°]; pmr (CCl_4) δ 8.02-7.71 (m, 2) and 7.61-7.36 ppm (m, 3).

4-Bromo-2-cyclopentenone, 14

This compound was prepared from 2-cyclopentenone (63) according to the method of DePuy *et al*. (64): bp 53-54° (2 mm) [lit. (64) bp 36-37° (0.1 mm)]; pmr (CCl_4) δ 7.70 (q, 1, J = 2.7 Hz and 5.7 Hz), 6.23 (q, 1, J = 1.5 Hz and 5.7 Hz), 5.11-5.36 (m, 1), and 3.30-2.37 ppm (m, 2).

2,5,5-Trideuterio-2-cyclopentenone

A mixture of cyclopentanone (60 g), 5 g of Na_2CO_3, and 350 mls of D_2O (80%) was heated to reflux for 3 hours. After cooling, the mixture was saturated with NaCl and extracted with Et_2O (3 x 200 mls). The ethereal extracts were combined and dried ($MgSO_4$) and the ether was removed by fractional distillation at atmospheric pressure. This procedure was repeated by reacting the remaining liquid with 99.6% D_2O to give 55 g of crude 2,2,5,5-tetradeuteriocyclopentanone. This crude material was converted to 2,5,5-trideuterio-2-cyclopentenone (25 g) which had 94% isotopic purity by the method of Garbisch (63): bp 49-50° (10 mm); pmr (CCl_4) δ 7.83-7.57 (m, 1) and 2.82-2.53 ppm (m, 2); mass spectrum (10.5 eV) *m/e* (rel intensity) 85 (94), 82 (6).

4-Bromo-2,5,5-trideuterio-2-cyclopentenone, 16

This compound was prepared from 2,5,5-trideuterio-2-cyclopentenone (94% iostopic purity) according to the method of DePuy *et al*. (64): bp 45-46° (1 mm); pmr (CCl_4) δ 7.63 (d, 1, J = 2.7 Hz) and 5.19 ppm (broad d, 1, J = 2.6 Hz).

3-Bromo-1-indanone

This compound was prepared from 1-indanone according to the method of Treibs and Schroth (65): mp 55-57° [lit. (65) mp 54°]; pmr (CCl_4) δ 7.74-7.18 (m, 4), 5.53 (q, 1, J = 3.4 Hz and 6.6 Hz), and 3.56-2.63 ppm (m, 2).

4-Pyrone, 24

This compound was prepared from chelidonic acid hydrate by the method of Willstater and Pummerer (66): mp 31-33° [lit. (66) mp 32.5°]; pmr (CCl_4) δ 7.85-7.60 (m, 1) and 6.42-6.17 ppm (m, 1).

2,6-Cycloheptadienone, 25

This compound was prepared from cycloheptanone by the method of Garbisch (63): bp 60-61° (2 mm) [lit. (63) bp 50.5-51.0° (1.0 mm)]; pmr (CCl_4) δ 6.79-5.74 (m, 1) and 2.43 ppm (t, 1, J = 3 Hz).

4,4,6,6-Tetramethylcyclohexenone

This compound was prepared from 2,2,4,4-tetramethylcyclohexanone (67) by bromination-dehydrobromination according to the method of Russell and Stevenson (30); bp 67-68° (5.4 mm) [lit. (30) bp 82-84° (15 mm)]; pmr (CCl_4) δ 6.44 (d, 1, J = 10.0 Hz), 5.63 (d, 1, J = 10.0 Hz), 1.73 (s, 2), 1.19 (s, 6), and 1.1 ppm (s, 6).

4,4-Dimethyl-2-cyclohexenone

This compound was prepared according to the method of Bordwell and Wellman (68): bp 55-57° (10 mm) [lit. (68) bp

42-43° (3 mm)]; pmr (CCl_4) δ 6.58 (d, 1, J = 10.0 Hz), 5.66 (d, 1, J = 10.0 Hz), 2.49-2.18 (m, 2), 1.99-1.65 (m, 2), and 1.15 ppm (s, 6).

4,4-Dimethylcyclohexadienone

A solution of 4,4-dimethylcyclohexenone (0.167 mole) and DDQ (0.184 mole) in 850 mls of dry benzene was heated to reflux for 21 hours. After cooling, the mixture was filtered and the filtrate was washed three times with $NaHSO_3$ and once with sat. $NaCO_3$. Removal of benzene by distillation at reduced pressure gave a red liquid which upon further distillation gave 10.5 g (63-71° at 4.0 mm) of a mixture consisting of 75% dienone [pmr (CCl_4) δ 6.8 (d, 1, J = 10 Hz), 6.03 (d, 1, J = 10 Hz), and 1.24 ppm (s, 3)] and 25% starting material. Since 4,4-dimethylcyclohexenone gave no ESR signal when reacted with basic DMSO under flow conditions, no attempt was made to separate these compounds.

6-Acetoxy-3,5,5-trimethyl-2-cyclohexenone, 51a

This compound was prepared according to the method of Ellis (38): mp 74-75° [lit. (38) mp 76-78°].

Cis and trans-6-acetoxy-3,5-dimethyl-2-cyclohexenone, 51b

3,5-Dimethyl-2-cyclohexenone was reacted with $Pb(OAc)_4$ as described in the general procedure for 72 hours to give a liquid consisting of 65% 51b and 35% starting enone (determined by pmr). Separation and purification was accomplished by glpc using a 10% QF-1 column (180°) which gave 51b as a mixture of the cis and trans isomers in a 1:1 ratio: ir (neat) 1731 (ester C=O), 1675 (C=O), 1622 (C=C), and 1224 cm^{-1} (C-O-C); pmr (CCl_4) δ 5.70 (broad s, 1), 5.07 (q, 1, J = 4.7 Hz (cis-doublet) and J = 12.5 Hz (trans-doublet)), 2.73-2.11 (m, 3), 2.09 (s, 3), 1.94 (s, 3), and 1.15-0.88 ppm (q, 3); mass spectrum (70 eV) m/e (rel intensity) 182 (1), 140 (5), 122 (105).

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

6-Acetoxy-2,4,4-trimethyl-2-cyclohexenone, 51c

2,4,4-Trimethyl-2-cyclohexenone was reacted with $Pb(OAc)_4$ as described in the general procedure for 72 hours to give a liquid consisting of 51c (85%) and starting enone (15%) as determined by pmr. Purification and separation was accomplished by glpc (10% QF-1 column at 170°) which gave 51c as a liquid that solidified on cooling: mp 46-47°; ir (liquid-neat) 1750 (ester C=O), 1688 (C=O), 1638 (C=C), and 1235 cm^{-1} (C-O-C); pmr (CCl_4) δ 6.36 (broad s, 1), 5.37 (t, 1, J = 10.0 Hz), 2.07 (s, 3), 1.97-1.76 (m, 2), 1.71 (d, 3, J = 1.5 Hz), 1.27 (s, 3), and 1.16 ppm (s, 3); mass spectrum (70 eV) m/e (rel intensity) 196 (2), 154 (5), 136 (22).

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

6-Acetoxy-4,4-dimethyl-2-cyclohexenone, 51d

4,4-Dimethyl-2-cyclohexenone was reacted with $Pb(OAc)_4$ as described in the general procedure for 54 hours giving a liquid consisting of 51d (61%) and starting enone (39%) as determined by pmr. Separation and purification of 51d was accomplished by glpc (10% QF-1 column at 165°). The pmr spectrum of 51d [(CCl_4) δ 6.71 (d, 1, J = 10.2 Hz), 5.87 (d, 1, J = 10.2 Hz), 5.45 (q, 1, J = 9.0 Hz and 11.0 Hz), 2.11 (s, 3), 2.6-1.9 (m, 2), 1.33 (s, 3), and 1.22 ppm (s, 3)] was identical to one previously reported (68). Although separation of larger quantities was possible by fractional distillation, the crude material could be reacted with basic DMSO since the starting enone gave no ESR signal under these conditions.

6-Acetoxy-4,4-diphenyl-2-cyclohexenone, 51e

4,4-Diphenyl-2-cyclohexenone was reacted with $Pb(OAc)_4$ as described in the general procedure for 70 hours giving a viscous liquid consisting of 51e (50%) and starting enone (50%) as determined by pmr. Chromatography of this mixture on silica gel and elution with hexane-methylene chloride (3:1 by volume) gave 51e as a solid. Crystallization from hexane (twice) gave a 30% yield of 51e as a milky white solid: mp 105-107°; ir (KBr) 1740 (ester C=O), 1681 (C=O), and 1220 cm^{-1} (C-O-C); pmr (CCl_4) δ 7.47 (broad s, 5), 7.29 (broad s, 6), 6.22 (d, 1, J = 10.0 Hz), 5.36 (q, 1, J = 6.0

Hz and 12.5 Hz), 3.09-2.60 (m, 2), and 2.07 ppm (s, 3); mass spectrum (70 eV) m/e (rel intensity) 306 (1), 264 (3), 246 (33), 220 (13), 218 (15).

Anal. Calcd for $C_{20}H_{18}O_3$: C, 78.41; H, 5.92. Found: C, 78.62; H, 5.97.

5-Methyl-2-cyclohexenone

Bromination-dehydrobromination of 3-methylcyclohexanone according to the method of Garbisch (63) gave a 30% combined yield of 5-methyl-2-cyclohexenone and 3-methyl-2-cyclohexenone in a 4:1 ratio as determined by pmr: bp 32-34° (0.8 mm). This mixture was used without further purification in the preparation of cis and trans-6-acetoxy-5-methyl-2-cyclohexenone.

Cis and trans-6-acetoxy-5-methyl-2-cyclohexenone

The mixture consisting of a 4:1 ratio of 5-methyl and 3-methyl-2-cyclohexenone was reacted with $Pb(OAc)_4$ as described in the general procedure for 48 hours to give a yellow liquid. Fractional distillation of this material gave a mixture of the cis and trans isomers of 6-acetoxy-5-methyl-2-cyclohexenone in an 8:6 ratio as a colorless liquid (65-67° at 0.1 mm). Further purification of this mixture was accomplished by glpc (10% QF-1 column at 170°); ir (neat) 1748 (ester C=O), 1690 (C=O), 1613 (C=C), and 1233 cm^{-1} (C-O-C); pmr (CCl_4) δ 7.06-6.61 (m, 1), 5.9 (q, 1), 5.42-4.82 (q, 1, J = 4.3 Hz (cis-doublet) and 12.5 (trans-doublet)), 2.78-2.14 (m, 3), 2.11 (s, 3), and 1.17-0.89 ppm (q, 3); mass spectrum (70 eV) *m/e* (rel intensity) 168 (1), 126 (13), 108 (44), 68 (100).

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

6-Acetoxy-2-cyclohexenone

2-Cyclohexenone (63) was reacted with $Pb(OAc)_4$ as described in the general procedure for 60 hours to give a liquid consisting of 75% acetoxy ketone and 25% starting enone as determined by pmr. Distillation of this liquid gave mainly the enone as the first fraction followed by the acetoxy ketone (40% yield): bp 82-83° (2.5 mm); ir (neat) 1732 (ester C=O), 1677 (C=O), 1608 (C=C), and 1232 cm^{-1} (C-O-C); pmr (CCl_4) δ 7.11-6.75 (m, 1), 6.08-5.80 (m, 1), 5.20 (q, 1, J = 6.6 Hz and 12.0 Hz), 2.77-1.81 (m, 4), and 2.07 ppm (s, 3); mass spectrum (70 eV) *m/e* (rel intensity) 154 (2), 112 (15), 94 (10).

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

Cis *and* *trans*-2-acetoxypulegone

Both isomers were prepared and separated (15% XF-1150 column at 168°) by the method of Zalkow and Ellis (69). The pmr spectra of the *cis* [δ 5.12 (d, 1, J = 5.5 Hz), 2.75-1.92 (m, 5), 2.1 (s, 3), 1.87 (s, 3), 1.77 (s, 3), and 0.97 ppm (d, 3, J = 7.0 Hz)] and *trans* [δ 4.67 (d, 1, J = 10.5 Hz), 3.03-1.5 (m, 5), 2.1 (s, 3), 1.83 (d, 3, J = 1.7 Hz), 1.77 (s, 3), and 1.04 ppm (d, 3, J = 6.0 Hz)] isomers (CCl_4) were consistent with those previously reported (70).

6-Acetoxy-2,4-cycloheptadienone, 58

Reaction of 3,5-cycloheptadienone (63) with 1.1 equivalents of $Pb(OAc)_4$ at room temperature for two hours followed by the usual workup (see general procedure) gave a mixture consisting of 50% tropone and 50% acetoxy ketone. When the reaction was carried out under conditions of reflux for 30 minutes, a mixture consisting of 95% tropone and 5% acetoxy ketone (determined by pmr) was obtained. Chromatography of the 50:50 mixture on silica gel and elution with hexane-ether (85:15 by volume) gave the acetoxy ketone in 95% purity as determined by pmr: uv max (95% EtOH) 285 mμ (ε 6500) and 223 mμ (ε 4400); ir (neat) 1740 (ester C=O), 1658 (C=O), 1637 (C=C), and 1232 cm^{-1} (C-O-C); pmr (CCl_4) δ 6.80-5.83 (m, 4), 5.67-5.30 (m, 1), 3.02-2.75 (m, 2), and 2.01 ppm (s, 3); mass spectrum (70 eV) m/e (rel intensity) 124 (1), 122 (1), 106 (7), 94 (4).

Anal. Calcd for $C_9H_{10}O_3$: C, 65.05; H, 6.07. Found: C, 65.30; H, 6.09.

Δ^3-2-Acetoxycaren-5-one, 62

Eucarvone was reacted with $Pb(OAc)_4$ as described in the general procedure for 80 hours to give a viscous liquid consisting of 62 and eucarvone (determined by pmr). Chromatography of this material on silica gel and elution with hexane-ethyl acetate (9:1 by volume) gave 62 (only one isomer) as a light yellow solid in 29% yield. Crystallization from hexane gave colorless crystals: mp 76-78°; ir (KBr) 1727 (ester C=O), 1650 (C=O), and 1240 cm^{-1} (C-O-C); pmr (CCl_4) δ 6.46-6.23 (m, 1), 5.51-5.30 (m, 1), 2.06 (s, 3), 1.78 (t, 3, J = 1.5 Hz), 1.72-1.41 (m, 2), 1.27 (s, 3), and 1.12 ppm (s, 3); mass spectrum (70 eV) *m/e* (rel intensity) 208 (1), 166 (50), 148 (150).

Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 69.05; H, 7.67.

Hydrolysis of 62

A solution of 62 (4.8 mmoles) and KOH (9.6 mmoles) in 150 mls of MeOH was heated to reflux for 15 minutes and cooled. After the addition of 250 mls of sat. NaCl, the mixture was extracted three times with 150 mls of Et_2O. The etheral extracts were combined, washed three times with 50 mls of H_2O and once with sat. NaCl, and dried ($MgSO_4$). After the removal of the ether at reduced pressure, the remaining yellow liquid was dissolved in 10 mls of CCl_4 and the resulting solution was cooled to -10° giving 0.32 g (45%) of Δ^3-2-hydroxycaren-5-one as colorless crystals (64): mp 82-85° [lit. (40) mp 84-86°]. Evaporation of the remaining solution to 0.5 ml followed by preparative glpc collection (15% FFAP column at 180°) gave 22 mg (3%) of

2,6,6-trimethyl-2-cycloheptene-1,4-dione (42), 68 [pmr (CCl_4) δ 6.42-6.29 (m, 1), 2.62 (s, 2), 2.53 (s, 2), 1.98 (d, 3, J = 2.0 Hz), and 1.13 ppm (s, 6)], approximately 2.3 mg (0.3%) of Δ^3-caren-2,5-dione (35), 66 [pmr (CCl_4) δ 6.47-6.32 (m, 1), 2.2 (s, 2), 1.93 (d, 3, J = 1.6 Hz), 1.37 (s, 3), and 1.33 ppm (s, 3)], and approximately 2.2 mg of 2,6,6-trimethylcycloheptane-1,4-dione (40), 69 [pmr (CCl_4) δ 2.82-2.13 (m, 3), 2.50 (s, 4), and 1.20-0.92 (t, 9); mass spectrum (70 eV) *m/e* (rel intensity) 168 (1), 150 (1) 148 (1), 83 (6)].

2-Acetoxy-3,4-dihydro-1-(2H)-naphthalenone, 91

α-Tetralone was reacted with $Pb(OAc)_4$ as described in the general procedure (72 hours) to give a yellow liquid consisting of 91 and α-tetralone. After the removal of α-tetralone by distillation (90-100° at 0.05 mm), the remaining viscous liquid was dissolved in ether and cooled to -78° resulting in the formation of a light yellow solid. Recrystallization of this material from hexane gave 91: mp 77-79° [lit. (71) mp 72-73°]; pmr (CCl_4) δ 8.06-7.82 (m, 1), 7.57-7.03 (m, 3), 5.37 (q, 1, J = 7.0 Hz and 11.0 Hz), 3.32-2.93 (m, 2), 2.43-2.12 (m, 2), and 2.1 ppm (s, 3).

2-Acetoxy-6,7-dimethyl-3,4-dihydro-1-(2H)-naphthalenone, 93

6,7-Dimethyl-3,4-dihydro-1-(2H)-naphthalenone was reacted with $Pb(OAc)_4$ as described in the general procedure for 72 hours to give a solid consisting predominately of 93 as determined by pmr. Chromatography of this material on silica gel and elution with hexane-ether (3:1 by volume) gave a light yellow solid which was crystallized from hexane to give colorless crystals of **93** in a 59% yield: mp 131-132°; ir (KBr) 1730 (ester C=O), 1686 (C=O), and 1247 cm^{-1} (C-O-C); pmr (CCl_4) δ 7.74 (s, 1), 6.82 (s, 1), 5.22 (q, 1, J = 7.0 Hz and 11.5 Hz), 3.13-2.78 (m, 2), 2.44-2.03 (m, 2), 2.24 (s, 6), and 2.12 ppm (s, 3); mass spectrum (70 eV) *m/e* (rel intensity) 190 (1), 172 (100), 161 (18), 146 (20).

Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.30; H, 6.81.

1,2,3,4-Tetrahydroisoquinoline-1,4-dione, **96**

This compound was prepared from ethyl phthalimidoacetate by the method of Caswell and Campbell (72): mass spectrum (20 eV) *m/e* M^+ = 161.

2H-1,2-Benzothiazin-4(3H)-one 1,1-dioxide, **97**

This compound was prepared from phenacyl saccharin by the method of Zinnes *et al*. (73, 74): mp 155-156° [lit. (74) mp 157-158°].

Phthalonimide, **99**

This compound was prepared from **96** by the method of Gabriel and Colman (75): mp 225-226° [lit. (75) mp 224°].

Carbindigo, **100**

This compound (blood red solid) was prepared from **96** by oxidation with H_2O_2 and $FeCl_3$ under acidic conditions by the method of Gabriel and Colman (76); however, the mass spectrum of this solid did indicate the presence of high molecular weight material (99 has a molecular weight of 318): (70 eV) m/e (rel intensity) 335 (3), 333 (5), 328 (2), 318 (1).

4-Tetrahydroquinolone, 104

This compound was prepared from p-toluenesulphonanilide and β-chloropropionic acid according to the method of Clemo and Perkin (77): mp 46-47° [lit. (77) mp 44°]; pmr ($CDCl_3$) δ 7.97-7.76 (m, 1), 7.47-7.13 (m, 1), 6.88-6.56 (m, 2), 4.60 (broad s, 1), 3.74-3.40 (m, 2), and 2.84-2.54 ppm (m, 2).

3-Acetoxy-4-chromanone, 108a

4-Chromanone was reacted with $Pb(OAc)_4$ as described in the general procedure for 68 hours to give a viscous liquid. When this liquid was dissolved in hot hexane and cooled to 0°, colorless crystals of 108a formed in a 30% yield. Recrystallization from hexane gave 108a in high purity: mp 80-81° [lit. (78) mp 74°]; pmr (CCl_4) δ 8.0-6.87 (m, 4), 5.62 (q, 1, J = 6.1 Hz and 11.0 Hz), 4.63-4.28 (m, 2), and 2.18 ppm (s, 3).

3-Acetoxy-4-thiochromanone, 108b

4-Thiochromanone was reacted with $Pb(OAc)_4$ as described in the general procedure for 36 hours to give a viscous liquid consisting of a 50:50 mixture of 108b and 4-thiochromanone. Chromatography of this material on silica gel and elution with hexane-methylene chloride (3:1 by volume) gave 108b as a light yellow solid which was crystallized from hexane to give faintly yellow crystals: mp 78-80°; ir (KBr) 1740 (ester C=O), 1690 (C=O), and 1232 cm^{-1} (C-O-C); pmr (CCl_4 - $CDCl_3$) δ 8.12-7.89 (m, 1), 7.50-6.96 (m, 3), 5.61 (q, 1, J = 5.0 Hz and 13.0 Hz), 3.77-2.84 (m, 2), and 2.14 ppm (s, 3); mass spectrum (70 eV) *m/e* (rel intensity) 222 (24), 180 (1), 162 (84), 135 (105).

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

$\Delta^{1,9}$-2-Octalone, 119a

This compound was prepared according to the method of Stork *et al.* (79): pmr (CCl_4) δ 5.67 (broad, s, 1) and 2.67-1.29 ppm (m, 13).

$\Delta^{1,9}$-4,4,7-Trimethyl-2-octalone, 119b

This compound was prepared from pulegone and ethyl acetoacetate according to the method of Chow and Quon (80). Purification of 119b was achieved by glpc (QF-1 column at 180°): pmr (CCl_4) δ 5.65 (broad s, 1), 2.67-1.11 (m, 8), 2.06 (s, 2), 1.03 (s, 5), and 0.93 ppm (s, 4); mass spectrum (70 eV) *m/e* (rel intensity) 192 (1), 190 (1), 177 (2), 136 (4).

$\Delta^{1,9}$-3-Acetoxy-2-octalone

$\Delta^{1,9}$-2-Octalone was reacted with $Pb(OAc)_4$ as described in the general procedure for 66 hours to give a mixture of the acetoxy ketone and enone. Chromatography of this material on silica gel and elution with hexane-ethyl acetate (85:15 by volume) gave separation of the acetoxy ketone as a viscous liquid which was dissolved in hot hexane. Upon cooling, crystals of the acetoxy ketone were formed in 15% yield. Recrystallization from hexane gave colorless crystals: mp 91-95°; ir (KBr) 1739 (ester C=O), 1677 (C=O), 1630 (C=C), and 1220 cm^{-1} (C-O-C); pmr (CCl_4) δ 5.70 (broad s, 1), 5.17 (q, 1, J = 5.7 Hz and 13.8 Hz), 2.7-1.15 (m, 11), and 1.06 ppm (s, 3); mass spectrum (70 eV) m/e (rel intensity) 208 (1), 166 (1), 148 (13), 122 (31).

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

$\Delta^{1,9}$-10-Methyl-2-octalone

This compound was prepared according to the method of Ross and Levine (81): bp 98-102° (0.4 mm) [lit. (81) bp 111-112° (2.5 mm)].

Cis and trans $\Delta^{1,9}$-3-acetoxy-10-methyl-2-octalone, 124

$\Delta^{1,9}$-10-Methyl-2-octalone was reacted with $Pb(OAc)_4$ as described in the general procedure for 72 hours to give a cis and trans mixture of 124 in addition to starting material. Chromatography of this reaction mixture on silica gel and elution with hexane-ether (4:1 by volume) gave 124 (cis and trans mixture) as a solid. When this solid was dissolved in hot hexane and cooled to 25°, one of the cis-trans isomers crystallized out in 95% purity and in 16% yield: mp 100-

102°; ir (KBr) 1740 (ester C=O), 1678 (C=O), 1618 (C=C) and 1227 cm^{-1} (C-O-C); pmr (CCl_4) δ 5.58 (broad, s, 1) 5.31 (q, 1, J = 8.5 Hz and 11.0 Hz), 2.5-1.42 (m, 10), 2.07 (s, 3), and 1.38 ppm (s, 3); mass spectrum (70 eV) *m/e* (rel intensity) 222 (2), 180 (5), 162 (6), 136 (90).

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

Further cooling (-10°) resulted in the crystallization of the other isomer in about 90% purity and in 17% yield: pmr (CCl_4) δ 5.63 (broad s, 1), 5.17 (q, 1, J = 8.5 Hz and 10.0 Hz), 2.60-1.47 (m, 10), 2.07 (s, 3), and 1.26 ppm (s, 3).

$\Delta^{1,2}$-3-Octalone, 130

$\Delta^{1,9}$-2-Octalone (25 g) was reduced (H_2, Pd-C) under conditions reported by Augustine (56) to give *cis* and *trans*-2-decalone in a 9:1 ratio. This mixture (20 g) was brominated (82) and dehydrobrominated (83) to give a mixture of both octalones and decalones as determined by pmr. Fractional distillation of this material gave 9.5 g of a mixture (octalones) consisting of about 60% *cis*-$\Delta^{1,2}$-3-octalone (the *cis* stereochemistry was assumed): bp 74-78° (0.4 mm); pmr (CCl_4) δ 6.67 (q, 1, J = 3.5 Hz and 10.0 Hz), 5.8 (q, 1, J = 1.5 Hz and 10.0 Hz), and a broad absorption from 2.70-1.30 ppm.

$\Delta^{1,2}$-4-Acetoxy-3-octalone, 131

The mixture containing about 60% *cis*-$\Delta^{1,2}$-3-octalone was reacted with $Pb(OAc)_4$ as described in the general procedure for 40 hours to give a mixture of compounds. The pmr of this material indicated the presence of at least four acetoxy methyl peaks. Chromatography of this material on silica gel and elution with hexane-ether (1:1 by volume) gave initially a liquid which solidified on cooling followed by a mixture (no attempt was made to analyze this material). The solid gave spectroscopic data consistent with structure 131: mp 59-66°; ir (liquid-neat) 1747 (ester C=O), 1690 (C=O), 1618 (C=C), and 1228 cm^{-1} (C-O-C); pmr (CCl_4) δ 6.91 (q, 1, J = 5.0 Hz and 10.0 Hz), 5.89 (d, 1, J = 10.0 Hz), 5.47 (d, 1, J = 13.0 Hz), 2.71-1.09 (m, 10), and 2.12 ppm (s, 3); mass spectrum (70 eV) *m/e* (rel intensity) 208 (3), 166 (1), 148 (4).

Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 68.95; H, 7.59.

10-Methyl-1-decalone

This compound (*cis* and *trans*) was prepared from $\Delta^{1,9}$-2-octalone according to a method originated by House *et al.* (57) and revised by Scanio and Mosbey.[6] The pmr spectrum of these isomers gave absorptions of the C-10 methyls at δ 0.79 and 1.01 in a 2:1 ratio, respectively.

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[6] *Ibid.*

$\Delta^{8,9}$-10-Methyl-1-octalone, 133

This compound was prepared from cis and trans-10-methyl-2-decalone by the method of Scanio and Mosbey in about 80% purity (the $\Delta^{2,3}$-isomer was also formed). The vinyl hydrogen absorbed as a triplet (J = 4.0 Hz) in the pmr spectrum at 6.11 ppm (δ) while the C-10 methyl gave a singlet at 0.99 ppm.

$\Delta^{9,10}$-Octaline-1,5-dione, 135

This compound was prepared from $\Delta^{9,10}$-octalindiol-1,5 (84) by an oxidation method of DePuy and Zaweski (85) in 43% yield: mp 111-112° [lit. (84) mp 113-114°].

$\Delta^{9,10}$-1-Octalone, 136

To a solution of 7.8 g of $\Delta^{9,10}$-octalol-1-acetate (84) in 150 mls of MeOH was added 4.9 g of NaOH. After stirring at 25° for two hours, the methanolic solution was concentrated at reduced pressure to about 25 mls and diluted with 200 mls of water. Three ether extracts (100 mls) of this solution were combined, washed with sat. NaCl and dried ($MgSO_4$). Removal of the ether at reduced pressure gave a liquid consisting (in part) of the desired $\Delta^{9,10}$-octalol-1 as determined by pmr. This crude alcohol (3 g) was dissolved in 20 mls of acetone. To this solution was added dropwise with stirring (0°) a solution of 1.1 equivalents of CrO_3 in 10 mls of water and 4 mls of conc. H_2SO_4. After stirring an additional hour, the mixture was warmed to room temperature and was diluted with 400 mls of water. Three methylene chloride extracts (100 mls) of this solution were combined and dried ($MgSO_4$). Removal of the methylene chloride at reduced pressure gave a liquid consisting of $\Delta^{9,10}$-1-octalone. Purification of this compound was accomplished by glpc (QF-1 column at 180°); ir (neat) 1660 (C=O) and 1629 cm^{-1} (C=C) [lit. (86) 1664 and 1634 cm^{-1}]; mass spectrum (70 eV) m/e = 150.

SOURCES OF CHEMICALS

<u>Chemical</u>	
N-Methyl-2-pyridone	Aldrich
Di-t-butyl ketone	Columbia
Benzophenone	Fisher Scientific
Di-isopropyl ketone	Columbia
Dimethylcyclobutenedione	Dr. J. S. Chickos
Isophorone	Aldrich
3,5-Dimethyl-2-cyclohexenone	Aldrich
2,4,4-Trimethyl-2-cyclohexenone	Dr. G. Stevenson
4,4-Diphenyl-2-cyclohexenone	Dr. G. Stevenson
Pulegone	Fluka
Tropolone	Aldrich
Eucarvone	D. Symalla
α-Tetralone	Aldrich
Thiochroman-4-one 1,1-dioxide	Dr. I. W. J. Still
N,N'-Dimethylindigo	Dr. G. Kaupp
N-Methylindigo	Dr. G. Kaupp
Indigo	Ciba
4-Chromanone	Aldrich
4-Thiochromanone	Aldrich
$\Delta^{4,5}$-5-Cholestane-3,6-dione	Dr. S. K. Malhotra
$\Delta^{1,9}$-10-Methyloctalin-2,8-dione	Dr. S. K. Malhotra
1-Indanone	J. T. Baker
Chelidonic acid hydrate	Aldrich

6,7-Dimethyl-3,4-dihydro-1-(2H)-naphthalenone (6,7-dimethyl-1-tetralone)	Chemical Samples
Ethyl phthalimidoacetate	Dr. D. Lamson
Phenacyl saccharin	Dr. D. Lawson
Dimethyl sulfoxide	MSA Research Corporation
Potassium t-butoxide	Baker

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