

1968

# Conformational studies of acyclic semidiones

Herbert Leon Malkus  
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CONFORMATIONAL STUDIES OF ACYCLIC SEMI-  
DIONES.**

**Iowa State University, Ph.D., 1968  
Chemistry, organic**

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CONFORMATIONAL STUDIES OF ACYCLIC SEMIDIONES

by

Herbert Leon Malkus

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

DOCTOR OF PHILOSOPHY

Major Subject: Organic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

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Dean of Graduate College

Iowa State University  
Of Science and Technology  
Ames, Iowa

1968

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Well, Memmius, I have taught you that things cannot be created out of nothing nor, once born, be summoned back to nothing. Perhaps, however, you are becoming mistrustful of my words, because these atoms of mine are not visible to the eye. Consider, therefore, this further evidence of bodies whose existence you must acknowledge though they cannot be seen.....

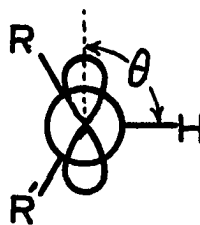
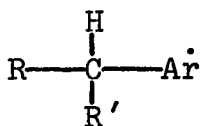
Lucretius  
The Nature of the Universe

## INTRODUCTION

The interaction between an alkyl hydrogen atom and an adjacent paramagnetic center has been known to obey a  $\cos^2\theta$  relationship. This relationship was first proposed by Symons (1) and expanded by Heller and McConnell (2) to explain the angle dependence of the  $\alpha$  hydrogen hyperfine splitting in the radical  $(\text{CO}_2\text{H})\text{CH}_2\dot{\text{C}}\text{HCO}_2\text{H}$  in solid succinic acid. The proposed equation is

$$a_{\alpha} = B_0 + B\cos^2\theta,$$

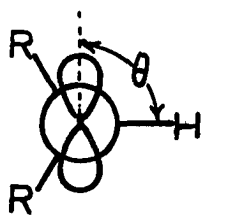
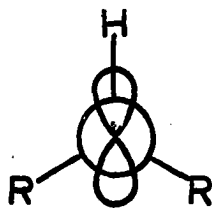
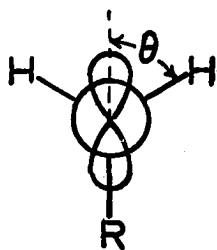
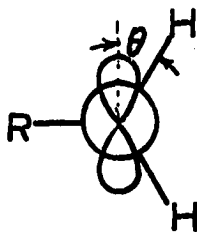
where  $a_{\alpha}$  is the hyperfine splitting constant of a hydrogen atom attached to a carbon adjacent to a planar  $\pi$  electron center.  $B_0$ , a constant, is regarded as small in comparison with the constant  $B$  (3). The term  $\theta$  is the angle between the carbon-hydrogen bond under investigation and the axis of the  $p_z$  orbital on the adjacent radical center (diagram 1).



1

Stone and Maki (4) studied the electron spin resonance spectra of nitroalkyl radical anions in solution. They introduced the concept of time averaged  $\cos^2\theta$  and suggested that

alkyl substituents assume an equilibrium conformation with a residual torsional motion. An  $\alpha$  methyl group is regarded as freely rotating with a time averaged  $\theta$  of  $45^\circ$ . Any deviation from  $a_\alpha$  for methyl groups is regarded as evidence for preferred conformation. As a consequence of the  $\langle \cos^2\theta \rangle$  relationship,  $\underline{R}$ , the ratio of  $\alpha$  hydrogen splitting to methyl hydrogen splitting, is directly related to  $\langle \cos^2\theta \rangle$  of the carbon-hydrogen bond under investigation. Projection diagrams for possible equilibrium conformations for  $R_2CH-Ar\cdot$  and  $RCH_2-Ar\cdot$  are shown in 2.

a  $\theta = 90^\circ$ b  $\theta = 0$ c  $\theta = 60^\circ$ d  $\theta = 30^\circ$ 

2

On the basis of the  $\cos^2\theta$  relationship,  $\underline{R}$  can be calculated for various values of  $\theta$ . For a  $\theta$  of  $0^\circ$ ,  $30^\circ$ ,  $60^\circ$ , and  $90^\circ$ ,  $\underline{R}$  assumes values of 2, 1.5, 0.5, and 0, respectively.

Table 1 contains a review of the literature for alkyl substituted radicals. This list of  $R$  values was adapted from Geske (5) and includes all radicals reported through May, 1968.

Table 1. Ratio,  $R$ , of  $\alpha$  hydrogen atom hyperfine splitting constant to methyl splitting constants for radicals in solution

Radical	$a_\alpha$ gauss	$R$	Solv.	Ref.
Nitromethane <sup>-</sup>	11.4	1.00		4
Nitroethane	9.75	0.85		4
Nitro-1-propane <sup>-</sup>	9.98	0.87		4
Nitro-2-propane	4.60	0.40		4
Nitro-2-butane	3.19	0.28		4
Methyl cyclooctatetraene <sup>-</sup>	5.1	1.00		6
Ethyl cyclooctatetraene	2.5	0.49		6
<i>n</i> -Propyl cyclooctatetraene <sup>-</sup>	2.5	0.49		6
4-Methylnitrobenzene	3.98	1.00	AN <sup>a</sup>	7
4,4'-Dinitrobenzene <sup>-</sup>	2.69	0.68	AN	8
4-Ethylnitrobenzene <sup>-</sup>	2.96	0.74	AN	5
4-Isopropylnitrobenzene <sup>-</sup>	1.74	0.44	AN	5
2-Methylnitrobenzene <sup>-</sup>	3.12	1.00	AN	5
2-Ethylnitrobenzene <sup>-</sup>	1.76	0.56	AN	5
2-Isopropylnitrobenzene <sup>-</sup>	1.13	0.36	AN	5
9-Methylanthracene <sup>-</sup>	4.27	1.00	DME <sup>b</sup> , THF <sup>c</sup>	9,10
9-Ethylanthracene <sup>-</sup>	2.5	0.58	DME, THF	11,10
9-Isopropylanthracene <sup>-</sup>	0.62	0.14	THF	10
9-Cyclopropylanthracene <sup>-</sup>	6.64	1.55	THF	10
9-Methylanthracene <sup>+</sup>	7.79	1.00	H <sub>2</sub> SO <sub>4</sub>	9,10
9-Ethylanthracene <sup>+</sup>	3.6	0.46	H <sub>2</sub> SO <sub>4</sub>	11,10
9-Isopropylanthracene <sup>+</sup>	0.62	0.14	H <sub>2</sub> SO <sub>4</sub>	10
9-Cyclopropylanthracene <sup>+</sup>	6.64	1.55	H <sub>2</sub> SO <sub>4</sub>	10
9,10-Dimethylanthracene <sup>-</sup>	3.88	1.00	DME	9
9,10-Diethylanthracene <sup>-</sup>	2.3	0.59	DME	11
9,10-Dimethylanthracene <sup>+</sup>	8.00	1.00	H <sub>2</sub> SO <sub>4</sub>	9
9,10-Diethylanthracene <sup>+</sup>	3.75	0.47	H <sub>2</sub> SO <sub>4</sub>	11

<sup>a</sup>Acetonitrile.

<sup>b</sup>1,2-Dimethoxyethane.

<sup>c</sup>Tetrahydrofuran.



Table 1 continued

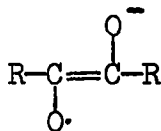
Radical	$a_{\alpha}$ gauss	$R$	Solv.	Ref.
4-Methylphenoxy	11.95	1.00	H <sub>2</sub> O	12
4-Ethylphenoxy	10.15	0.85	H <sub>2</sub> O	12
4-n-Propylphenoxy	8.7	0.73	H <sub>2</sub> O	12
4-Isopropylphenoxy	6.0	0.50	H <sub>2</sub> O	12
2,6-Dimethylphenoxy	6.5	1.00	H <sub>2</sub> O	12
2,6-Diethylphenoxy	5.7	0.88	H <sub>2</sub> O	12
2,6-Diisopropylphenoxy	3.7	0.57	H <sub>2</sub> O	12
2,6-Di-t-butyl-4-methylphenoxy	10.7	1.00	C <sup>d</sup>	13
2,6-Di-t-butyl-4-ethylphenoxy	9.0	0.80	C	13
9-Methylxanthy	12.16	1.00		14
9-Ethylxanthy	6.20	0.51		14
9-Isopropylxanthy	<1	<0.08		14
9-sec-Butylxanthy	<1	<0.08		14
1,4-Dimethylnaphthalene <sup>-</sup>	3.26	1.00	THF	10
1,4-Dicyclopropylnaphthalene <sup>-</sup>	4.77	1.46	THF	10
1-Phenylpropane-1,2-semidione <sup>-</sup>	3.43	1.00	80/20 <sup>e</sup>	15
1-Phenylbutane-1,2-semidione <sup>-</sup>	3.38	0.99	80/20	15
1-Phenyl-3-methylbutane-1,2-semidione <sup>-</sup>	1.45	0.42	80/20	15
Butane-2,3-semidione <sup>-</sup>	5.70	1.00	DMSO <sup>f</sup>	16
Hexane-3,4-semidione <sup>-</sup>	4.90	0.86	DMSO	16
Octane-4,5-semidione <sup>-</sup>	4.60	0.81	DMSO	16
2,7-Dimethyloctane-4,5-semidione <sup>-</sup>	4.30	0.76	DMSO	16
2,5-Dimethylhexane-3,4-semidione <sup>-</sup>	2.0	0.35	DMSO	16
Methyl-t-butyl nitroxide	12.7	1.00		17
Ethyl-t-butyl nitroxide	9.8	0.77		17
Isopropyl-t-butyl nitroxide	1.8	0.14		17

<sup>d</sup>Cyclohexane.

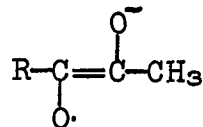
<sup>e</sup>80% Dimethyl sulfoxide-20% t-butanol.

<sup>f</sup>Dimethyl sulfoxide.

The radicals discussed in this work are semidione radical anions of the type 3 and 4.



3



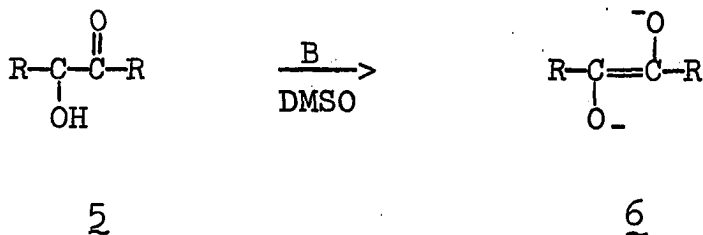
4

R is either a cyclic or acyclic alkyl group. The chemistry of semidiones has been the subject of numerous review articles (16, 18, 19).

## RESULTS AND DISCUSSION

## Dicycloalkyl Semidiones

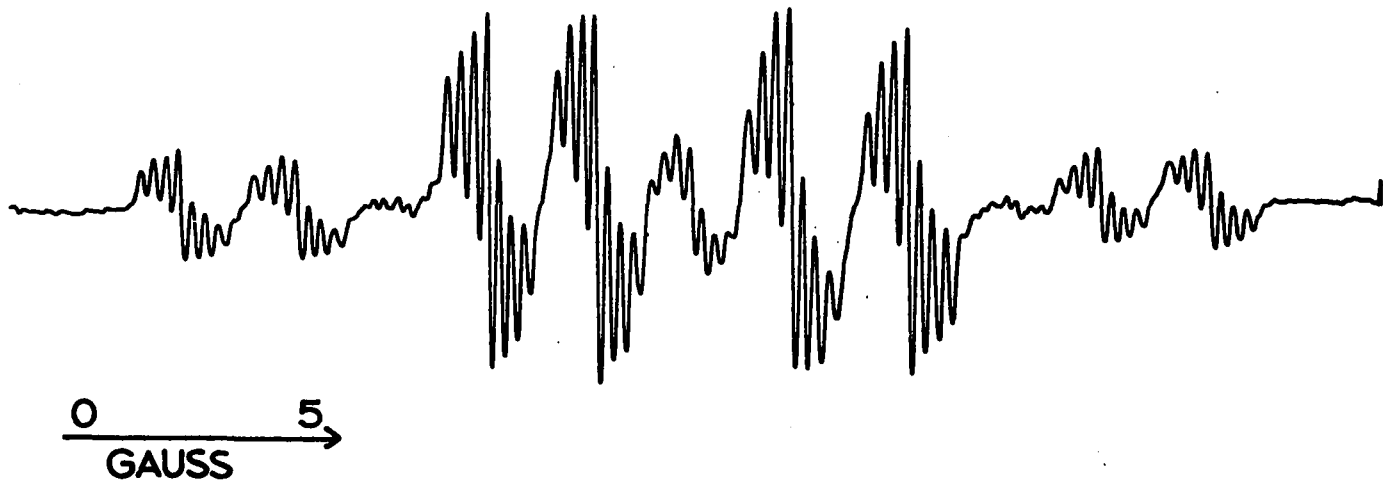
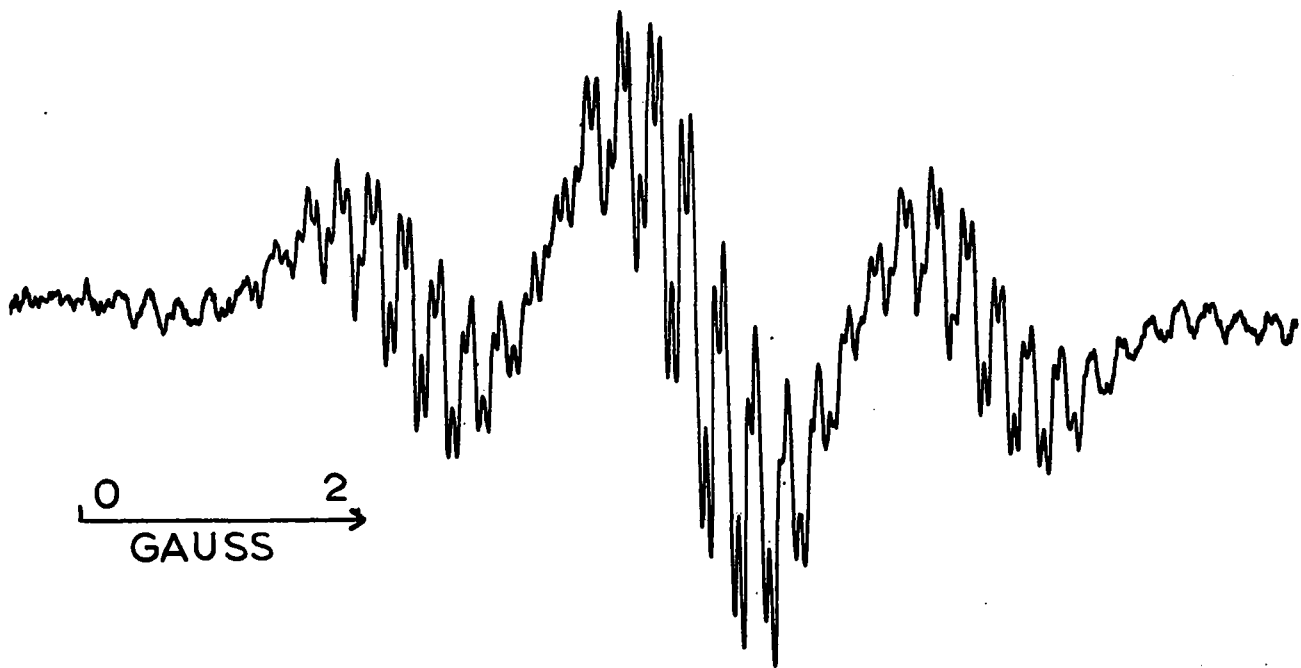
Semidiones are generated from  $\alpha$ -hydroxyketones by action of a strong base in dimethyl sulfoxide (DMSO).



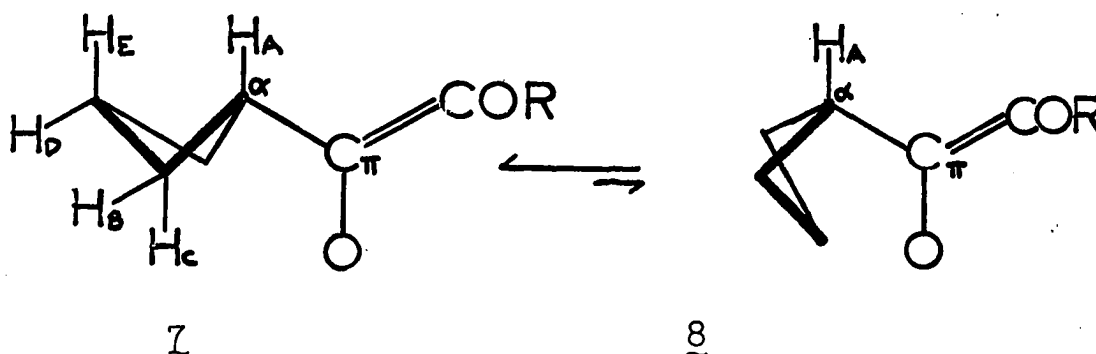
The mechanism of the reaction is unknown. This is due to the experimental requirement of low concentration (less than 0.1 molar) in order to obtain well resolved ESR spectra. Semidiones from 1,2-dialkylethan-ol-ones, 5, are properly named as 1,2-dialkylethanesemidiones, 6, and will be referred to as dialkyl semidiones. The first radical studied, 1,2-dicyclobutylethanesemidione, therefore, will be referred to as dicyclobutyl semidione. The corresponding  $\alpha$ -hydroxyketone is referred to as dicyclobutyl acyloin.

Dicyclobutyl acyloin was prepared via the acyloin condensation of ethyl cyclobutanecarboxylate in sodium and ether. When added to a degassed solution of potassium t-butoxide in DMSO, dicyclobutyl acyloin generated dicyclobutyl semidione (Figure 1a). On simulation, the spectrum arises from two hydrogens with splitting constant 2.22 gauss; four hydrogens, 0.45 gauss; four hydrogens, 0.23 gauss; and two hydrogens, 0.08 gauss. The spectrum was analyzed by the

Figure 1. (a) First-derivative ESR spectrum of dicyclobutyl semidione (top) in DMSO.  
(b) First-derivative ESR spectrum of cyclobutylmethyl semidione.



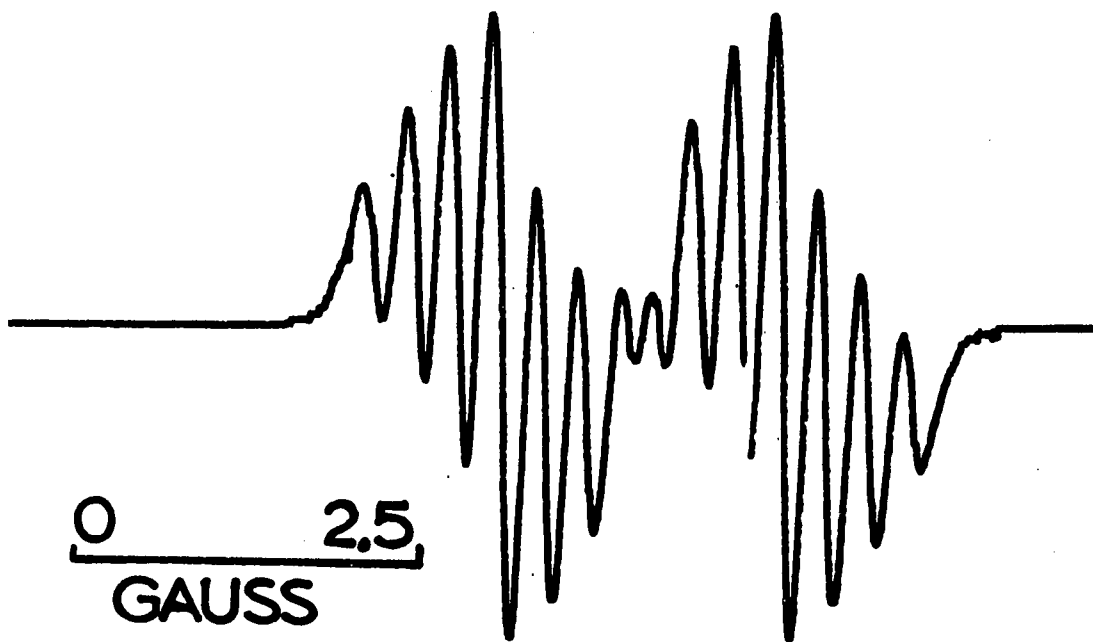
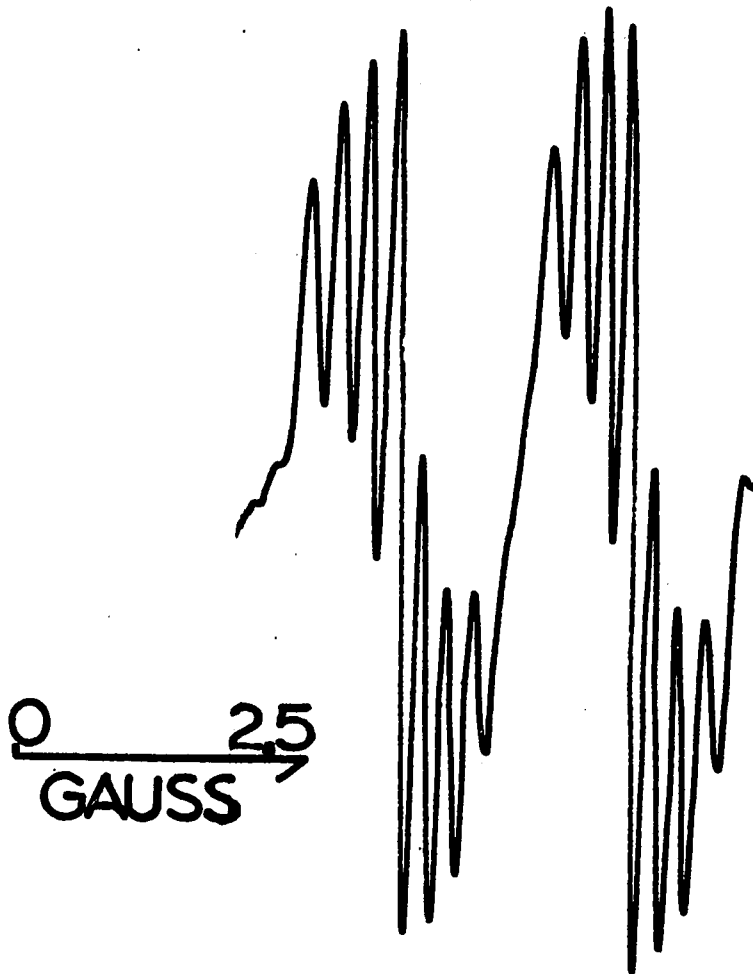
synthesis of cyclobutyl methyl acryloin. The semidione generated therefrom displayed a large quartet splitting of 5.55 gauss for the methyl group, a doublet of 2.11 gauss for the  $\alpha$  methine hydrogen atom, a triplet of 0.44 gauss for two  $\beta$  hydrogens, and a triplet of 0.23 gauss for the other two  $\beta$  hydrogens (Figure 1b, 2). The assignment of the 0.44 or 0.45 gauss hyperfine splitting constants (hfsc) is based upon the well founded double V interaction (20-22).



The large  $\beta$  hfsc are due to the vicinal hydrogen atom ( $H_B$ ) cis to the  $\alpha$  methine hydrogen. Similarly the 0.08 gauss splitting is due to  $H_D$  in 7. This hydrogen atom lies in a two and a half V arrangement with respect to the  $\pi$  electron cloud in the semidione systems.

Cyclobutane has been shown to be puckered  $35^\circ$  (23-25). Such a conformation would place both protons  $H_B$  and  $H_D$  in a psuedo equatorial position. Cyclobutane itself undergoes rapid interconversion of two puckered conformations. In dicyclobutyl semidione apparently conformation 7 is populated

Figure 2. Expansion of a center line in the first-  
derivative ESR spectrum of cyclobutyl methyl  
semidione (top) in DMSO; calculated spectrum  
(bottom) for Lorentzian linewidth of 0.2  
gauss and splitting constants from text  
performed by JEOLCO JNM-RA-1 spectrum  
accumulator.





to the exclusion of 8.

The large doublet splitting of methyl cyclobutyl semidione and the large triplet splitting of dicyclobutyl semidione are assigned to the methine cyclobutyl hydrogen atoms. The magnitude of the hfsc reflects a small conformational preference between the  $H_{\alpha}-C_{\alpha}-C_{\pi}$  plane and the  $p^z$  orbital  $-C_{\pi}-C_{\alpha}$  planes.

Cyclopentane rings have also been shown to exist in a folded or puckered conformation (26,27). As in the case of cyclobutane, cyclopentane undergoes rapid interconversion of two conformers. In dicyclopentyl semidione, conformation 9 is more highly populated than 10. The semidione displayed a striking signal composed of a large triplet of 1.92 gauss, each line of which is split into 17 equally spaced lines (Figure 3a). The spectrum was analysed by synthesis of cyclopentyl methyl acyloin. The semidione of the latter displayed a large quartet of 5.77 gauss for the methyl group, a doublet of 1.92 gauss for the  $\alpha$  methine hydrogen atom, a triplet of 0.44 gauss for the two  $\beta$  hydrogens, a triplet of 0.22 gauss for the other two  $\beta$  hydrogens, and a small triplet of 0.11 gauss for two  $\gamma$  hydrogens (Figure 3b, 4). Assignments of the splitting constants were made using the established two-V interactions. The large triplet splitting is assigned to the pair of  $\beta$  hydrogen ( $H_B$ ) cis to the  $\alpha$  methine ( $H_A$ ) hydrogen atom. The 0.22 gauss triplet is assigned to the second pair

Figure 3. (a) First-derivative ESR spectrum of dicyclopentyl semidione (top) in DMSO.

(b) First-derivative ESR spectrum of cyclopentyl methyl semidione (bottom) in DMSO.

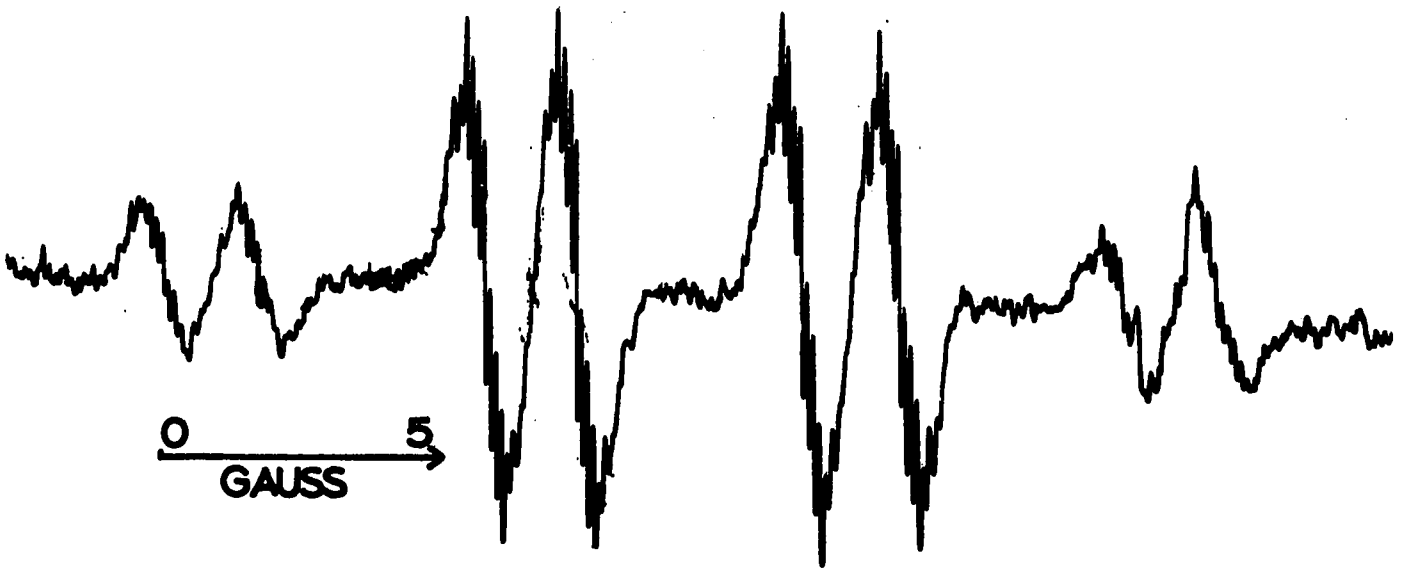
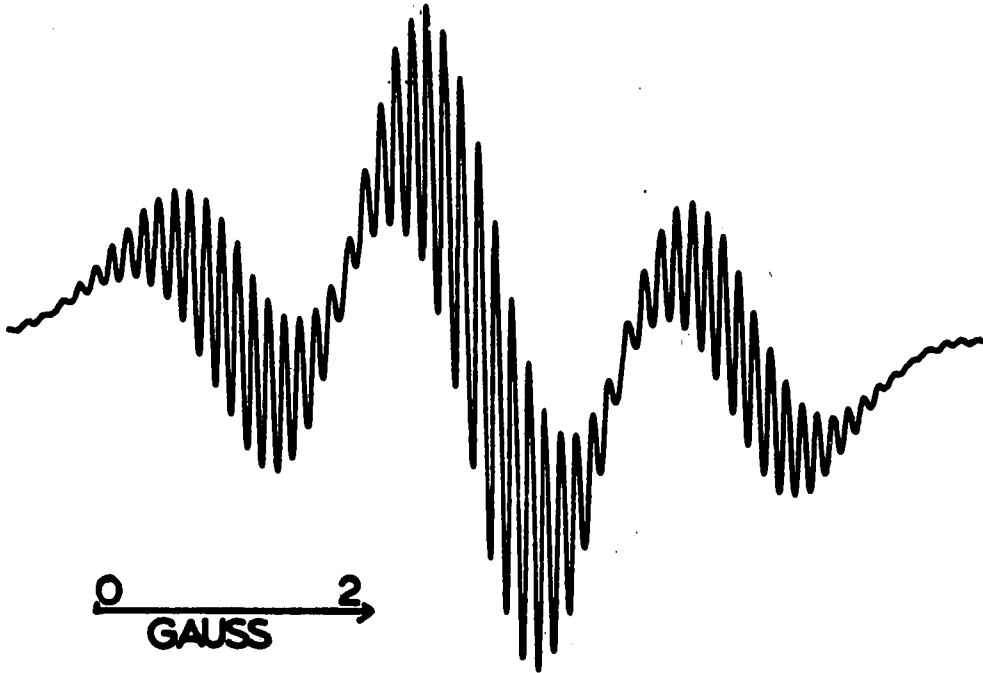
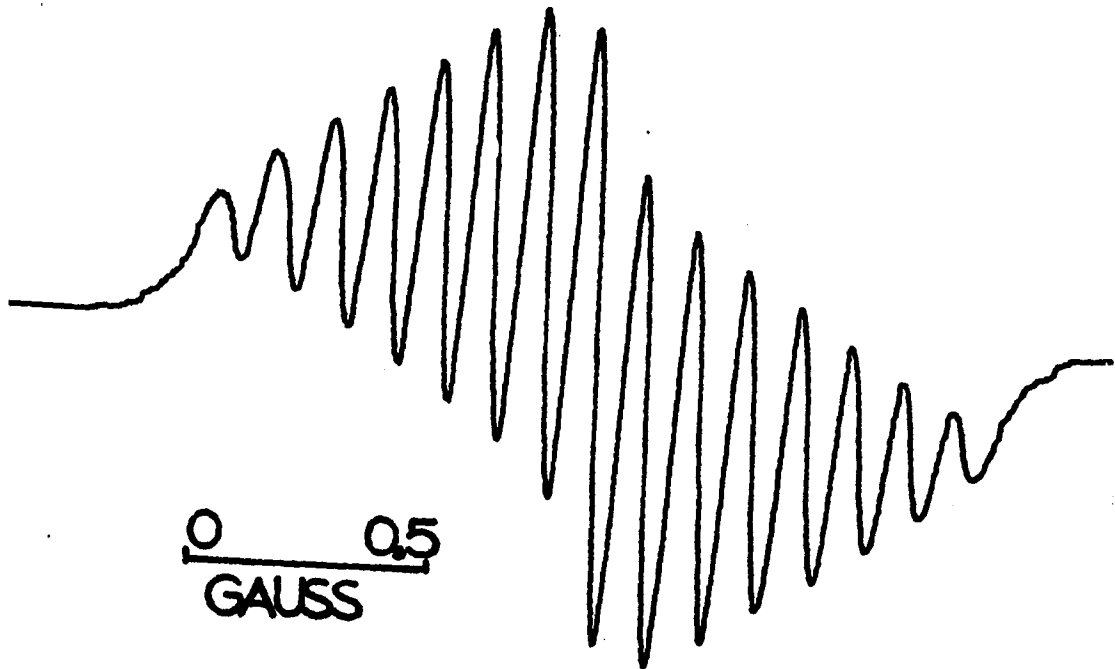
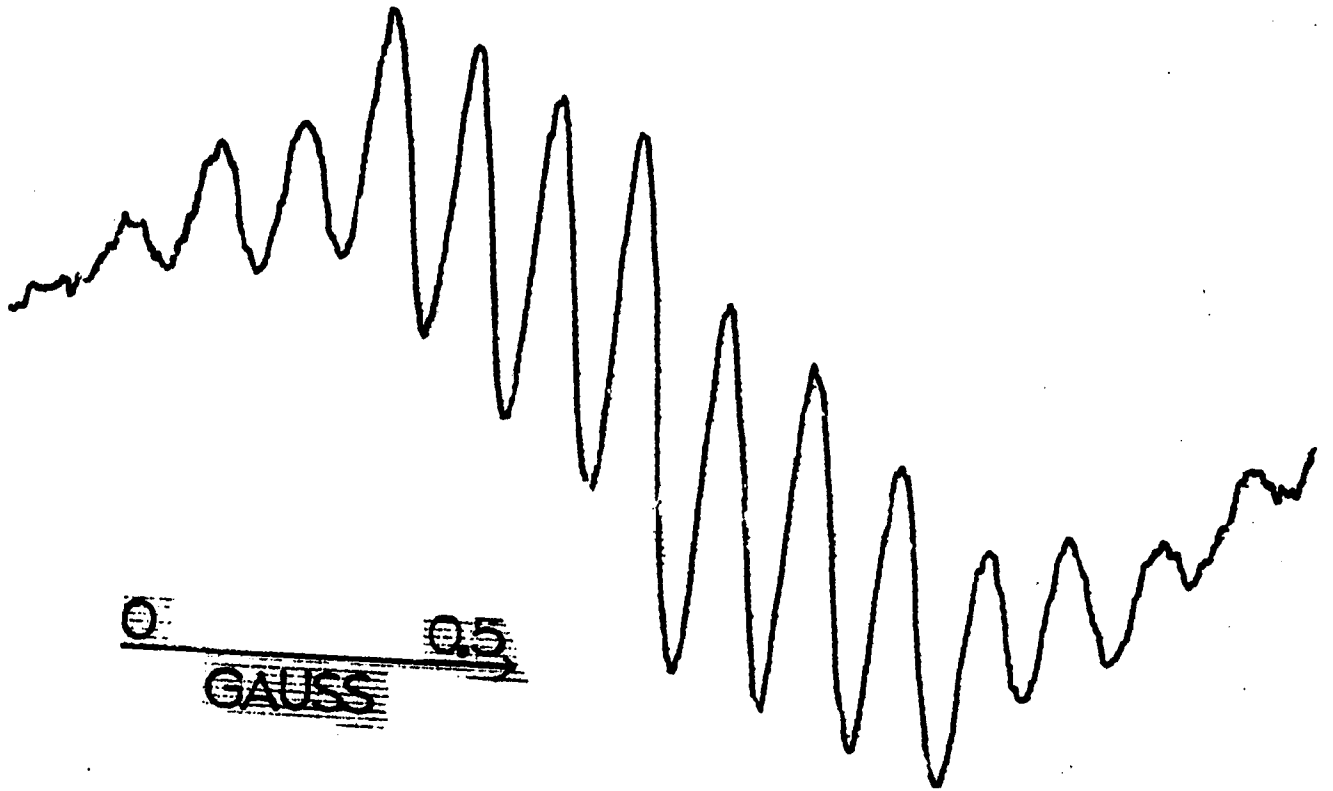
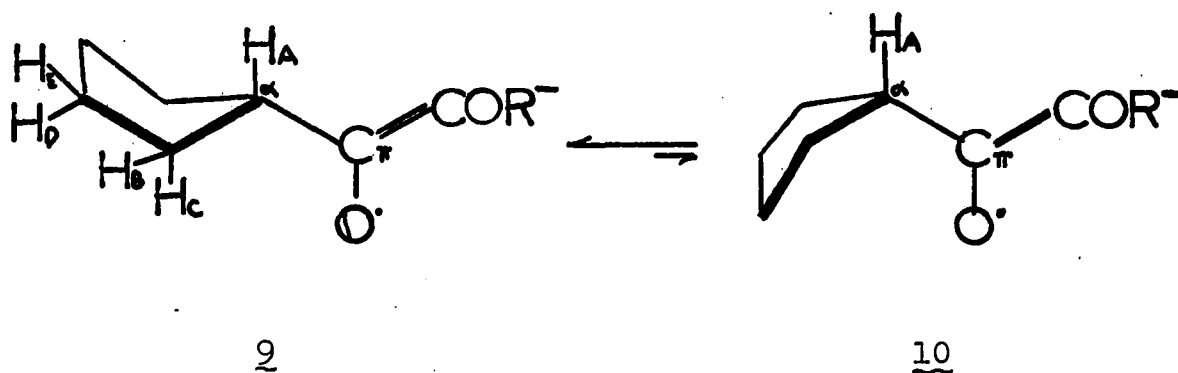


Figure 4. Expansion of a center line in first-derivative ESR spectrum of cyclopentyl methyl semidione (top) in DMSO; calculated spectrum (bottom) for Lorentzian linewidth at 0.2 gauss and splitting constants from text performed by JEOLCO JNM-RA-1 spectrum accumulator.





of  $\beta$  hydrogens ( $H_C$ ), and the small triplet is assigned to the  $\gamma$  hydrogens ( $H_D$ ) trans to the  $\alpha$  methine hydrogen atom. The splitting constants for dicyclopentyl semidione (a 1.92 gauss triplet, a 0.44 gauss pentet, a 0.22 gauss pentet, and a 0.11 gauss pentet) are assigned to hydrogen atoms  $H_A$ ,  $H_B$ ,  $H_C$ , and  $H_D$ , respectively.

Dicyclohexyl semidione displays a triplet splitting of 1.88 gauss. The fine structure can be observed at room temperature but cannot be resolved (Figure 5a). The spectrum of cyclohexyl methyl semidione (Figure 5b) consists of a large quartet splitting of 5.73 gauss, a doublet splitting of 1.73 gauss, and a well resolved pentet of 0.30 gauss split into pentets of 0.08 gauss (Figure 6). The quartet is due to the semidione methyl hydrogens, and the doublet corresponds to the  $\alpha$  methine hydrogen atom. The two pentet splitting, caused by two sets of four equivalent hydrogens cannot be definitively assigned. The semidione exists as a frozen chair conformation (28) with

Figure 5. (a) First-derivative ESR spectrum of dicyclohexyl semidione (top) in DMSO.  
(b) First derivative ESR spectrum of cyclohexyl methyl semidione (bottom) in DMSO.

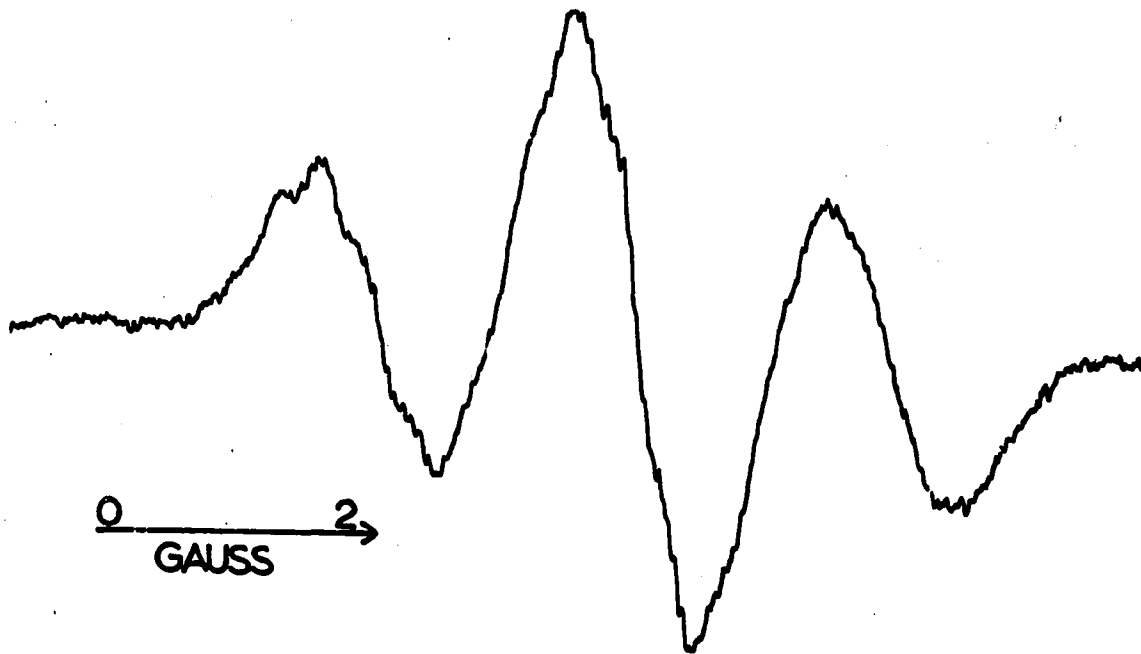
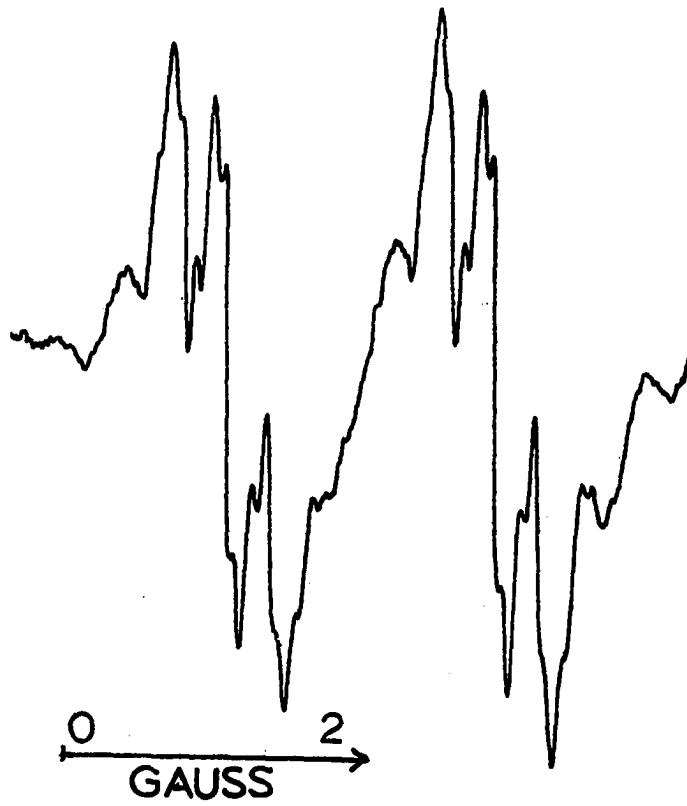


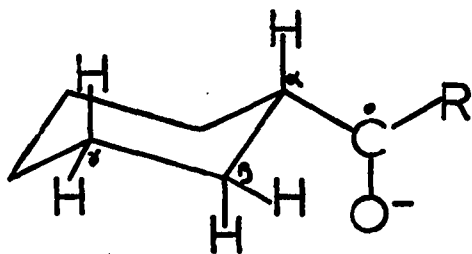
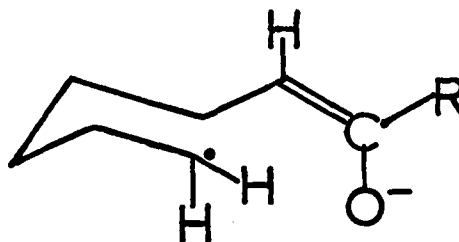


Figure 6. Expansion of two center lines in the first-  
derivative ESR spectrum of cyclohexyl methyl  
semidione in DMSO.

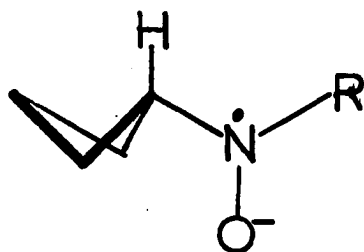
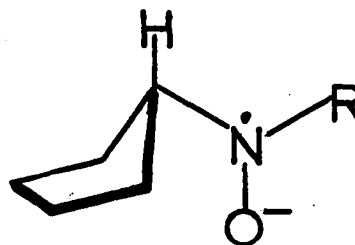


respect to  $\tau_0$ , the period of  $\beta$  hydrogen interaction ( $10^{-8}$  sec).

One interpretation of the spectrum is the assignment of the large pentet splitting to the four  $\beta$  hydrogen atoms. Hyperconjugative resonance structures such as 12 might explain the equivalence of the  $\beta$  hydrogen atoms. This view has been

1112

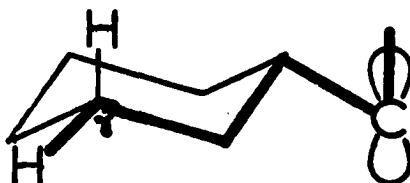
partly substantiated in a private communication from Dr. T. A. J. W. Wajer (29) and unpublished results of Drs. A. Mackor, T. A. J. W. Wajer, and T. J. deBoer concerning dicyclohexyl nitroxide. Nitroxide radicals are comparable to semidiones in that alkyl substituents display similar conformational preferences. Dicyclobutyl nitroxide, structure 13, displays an  $\alpha$  methine hydrogen splitting constant of 4.5 gauss and  $\beta$  hydrogen splitting constants of 0.95 gauss and 0.34 gauss.

1314

The corresponding constants of dicyclopentyl nitroxide (structure 14) are 4.7, 0.87, and 0.44 gauss. These splittings are approximately twice the magnitude of the corresponding semidione hyperfine splittings. When the 12.7 gauss splitting constant for the  $\alpha$  methyl hydrogens in methyl t-butyl nitroxide is compared with 5.70 gauss for the methyl hydrogens in dimethyl semidione, it becomes apparent that the same conformational effects are operating in both systems. A ratio, R, between the  $\alpha$  hydrogen atom splitting constant and the corresponding methyl hydrogen splitting constant has been used as a measure for conformational preference. R values of 0.35 and 0.37 gauss for dicyclobutyl and dicyclopentyl nitroxide correlate well with 0.38 and 0.34 for dicyclobutyl and dicyclopentyl semidione, respectively. Taking into account these apparent similarities, it is assumed that the spectra of cyclohexyl-t-butyl nitroxide and cyclohexyl methyl semidione would be comparable. The assigned  $\beta$  hydrogen splitting

constants of the nitroxide (0.71 gauss (30); 0.85 and 0.42 gauss (31)) have been refuted by Dr. Wajer. Deuterium substitution studies of cyclohexyl-t-butyl nitroxide have indicated that the axial and equatorial  $\beta$  hydrogen atoms are equivalent. However, these experiments have also shown that only two  $\gamma$  hydrogen atoms are equivalent.

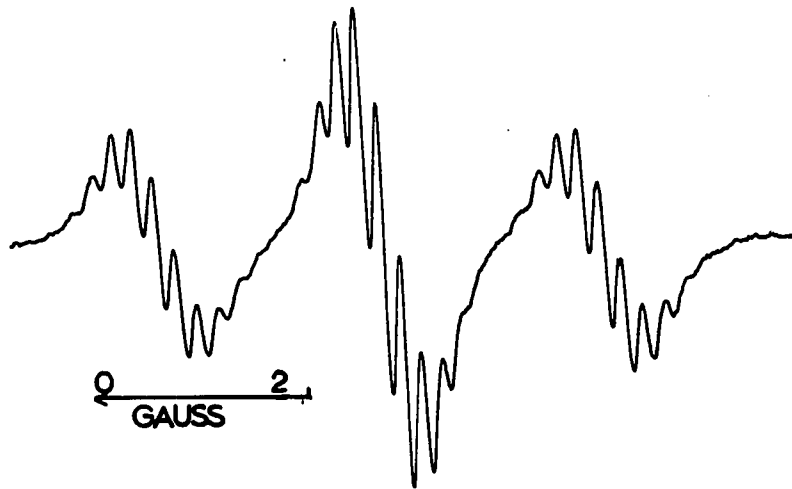
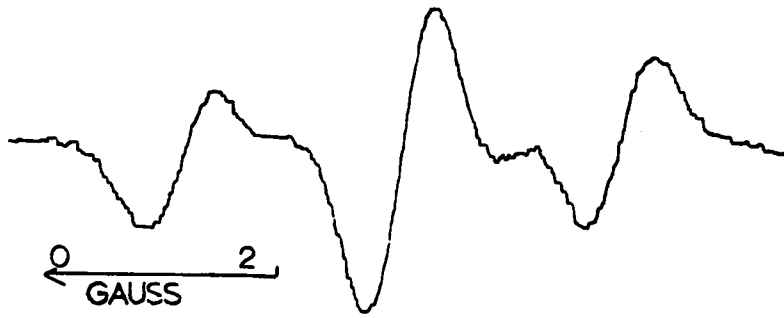
Another interpretation of the data for cyclohexyl methyl semidione invokes a two and a half V interaction between the semidione system and the  $\gamma$  equatorial hydrogens (15). The two  $\beta$  equatorial and the two  $\gamma$  equatorial hydrogen atoms might be equivalent leaving a corresponding set of four equivalent axial hydrogen atoms.



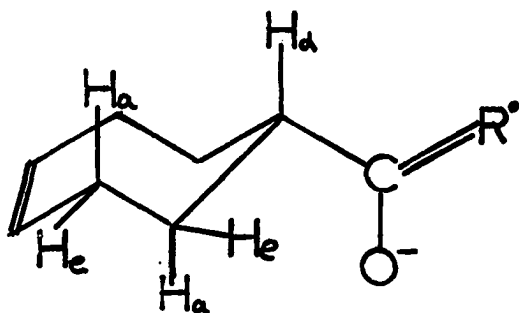
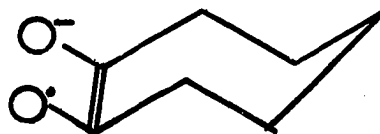
15

Dicycloheptyl semidione exhibits a simple triplet spectrum with an hfsc of 1.95 gauss (Figure 7a). This spectrum is similar in appearance to that of dicyclohexyl semidione in that fine splitting is present but cannot be resolved.

Figure 7. (a) First-derivative ESR spectrum of dicycloheptyl semidione (top) in DMSO.  
(b) First-derivative ESR spectrum of di-4-cycloheptenyl semidione (bottom) in DMSO.



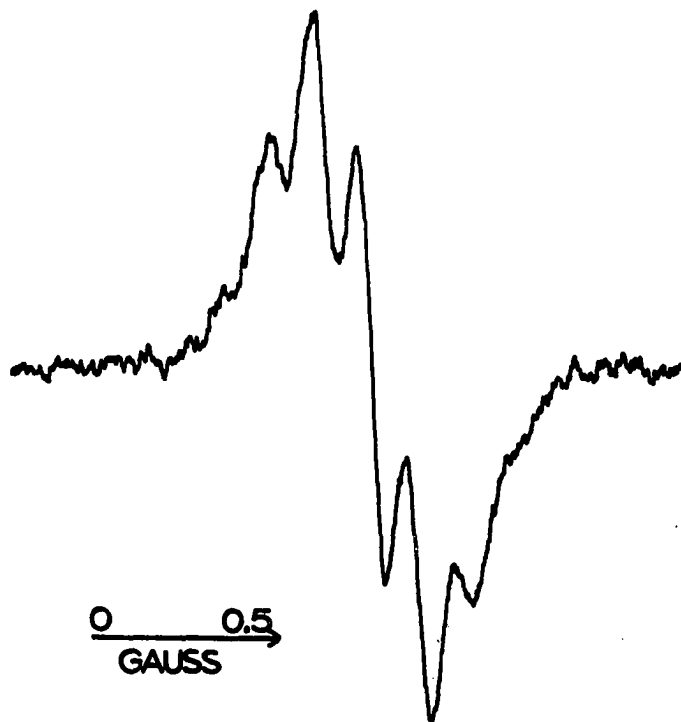
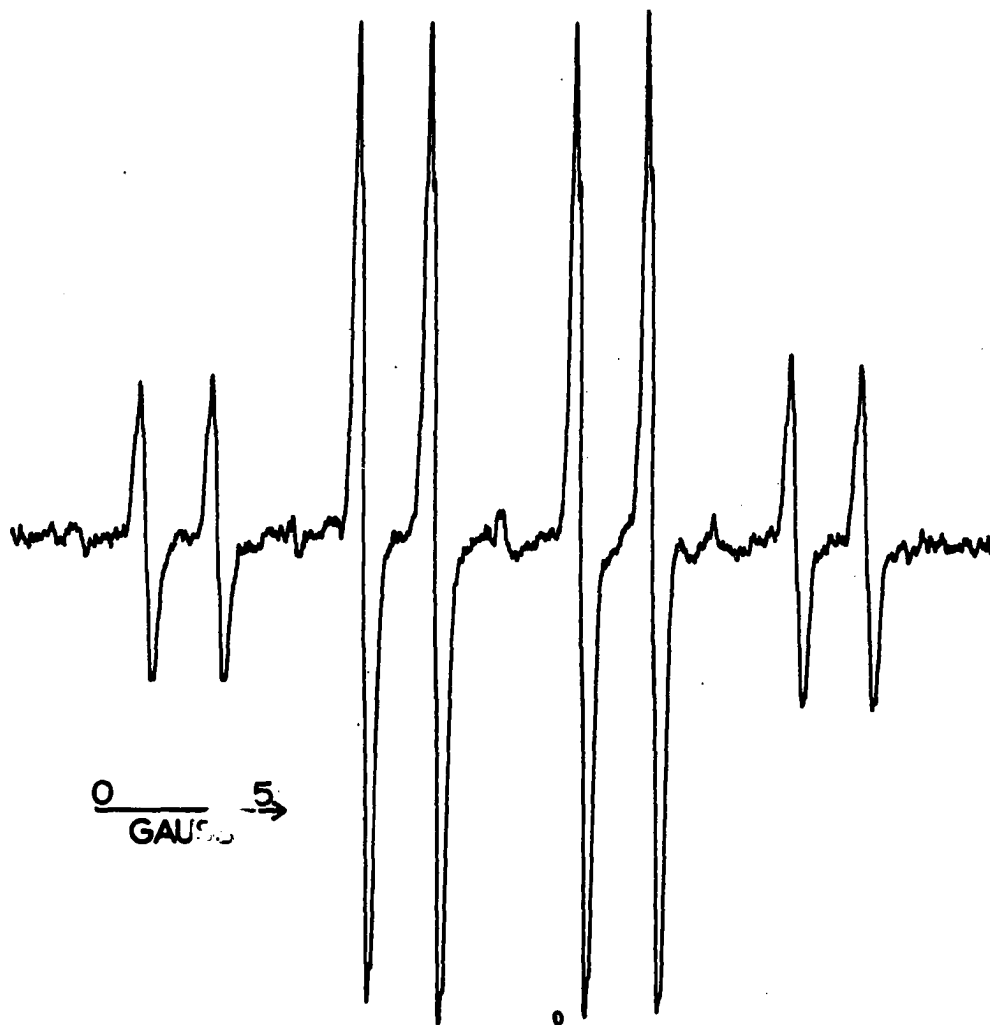
Di-4-cycloheptenyl semidione displays a spectrum consisting of a triplet of nonets (Figure 7b). The large triplet splitting of 2.08 gauss is due to the  $\alpha$  methine hydrogens. The small nonet of 0.18 gauss is caused either by the equivalence of the 8  $\beta$  hydrogen atoms or the equivalence of 4  $\beta$  equatorial and 4  $\gamma$  equatorial hydrogen atoms (structure 16). Cycloheptane semidione displays a triplet of triplets, indicating a frozen chair-like conformation as in 17 (32). Therefore, both the cycloheptyl and 4-cycloheptenyl rings in the dicycloheptyl and di-4-cycloheptenyl semidione are expected to assume stable chair conformations with respect to  $\tau_0$ .

1617

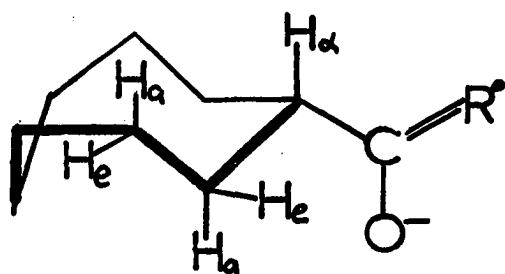
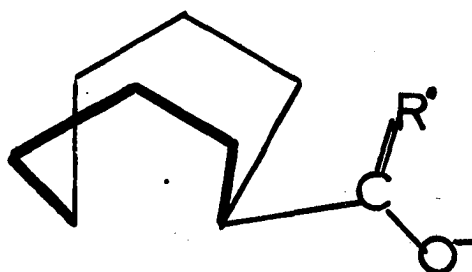
Cyclooctyl methyl semidione exhibits a basic quartet of doublets (Figure 8). The quartet of 5.85 gauss is due to the methyl group, and the doublet of 1.94 gauss is assigned to the  $\alpha$  methine hydrogen atom. Further splitting is observed



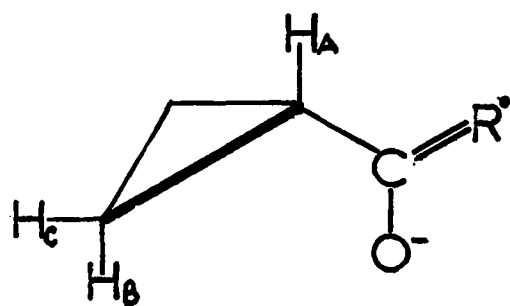
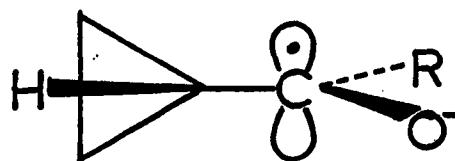
Figure 8. First-derivative ESR spectrum of cyclooctyl methyl semidione (top) in DMSO; expansion of a center line (bottom) in the above spectrum.



in the form of a pentet of 0.09 gauss. The small pentet splitting is assigned either to the  $\beta$  ring hydrogens or to two  $\beta$  equatorial hydrogens and two  $\gamma$  equatorial hydrogens. This is evidence that cyclooctane rings are rapidly inverting (32-34). However, substituted cyclooctanes have been studied by NMR at low temperatures indicating a possible preferred conformation (35). The preferred conformation, a half crown 18, is not energetically favored over 19 or 20. Therefore, it is possible that at 30° rapid psuedo rotation is occurring causing equilibration of the hydrogens. However, this is not demanded, and the interpretation of this spectrum must await deuterium substitution studies.

181920

Dicyclopropyl semidione displayed a 21 line spectrum only 3.5 gauss in width (Figure 9a). The predominant triplet observed in dicyclohexyl semidione, dicyclobutyl semidione, and other members of the series is not obvious from inspection of the spectrum of dicyclopropyl semidione. Therefore, cyclopropyl methyl semidione was prepared to aid in the interpretation. The ESR spectrum exhibited by this radical is shown in Figures 9b and 10 and consists of a major quartet of 5.88 gauss, a doublet of 0.57 gauss, a triplet of 0.37 gauss, and a triplet of 0.20 gauss. The doublet of 0.57 gauss is attributed to the  $\alpha$  methine hydrogen ( $H_A$ ), diagram 21.

2122

The 0.37 gauss doublet is assigned to the methylene hydrogens ( $H_C$ ) cis to  $H_A$ , and the small doublet of 0.20 gauss is due to the two remaining hydrogen atoms ( $H_B$ ). The corresponding hfsc for dicyclopropyl semidione are a triplet of 0.57 gauss, a pentet of 0.37 gauss, and a smaller pentet of 0.19 gauss. These hfsc are attributed to hydrogen atoms  $H_A$ ,  $H_C$ , and  $H_B$ ,

Figure 9. (a) First-derivative ESR spectrum of dicyclopropyl semidione in DMSO.

(b) First-derivative ESR spectrum of cyclopropyl methyl semidione in DMSO.

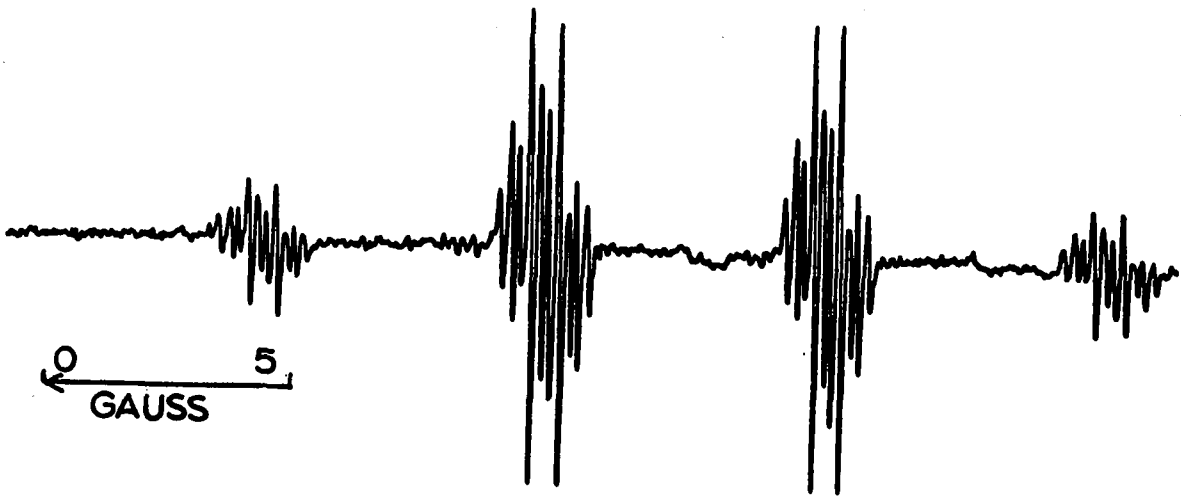
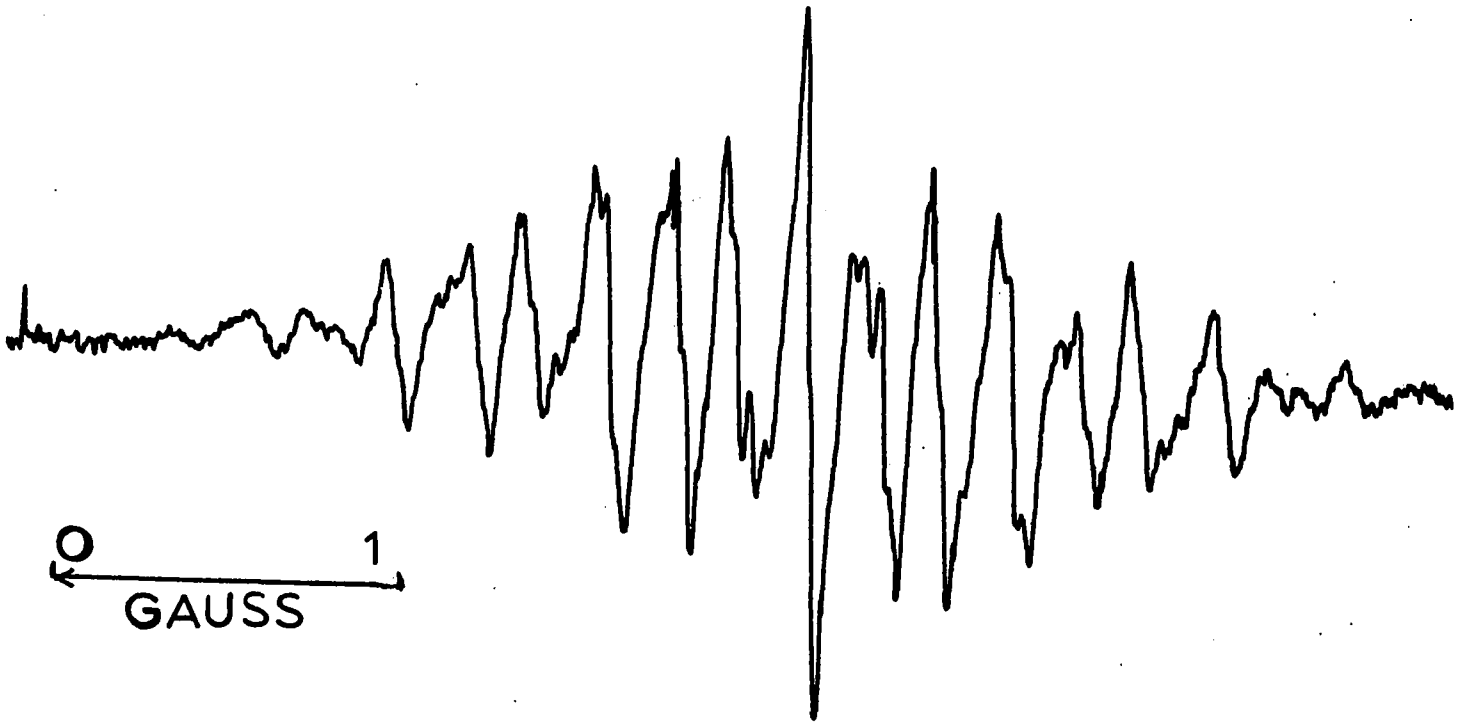
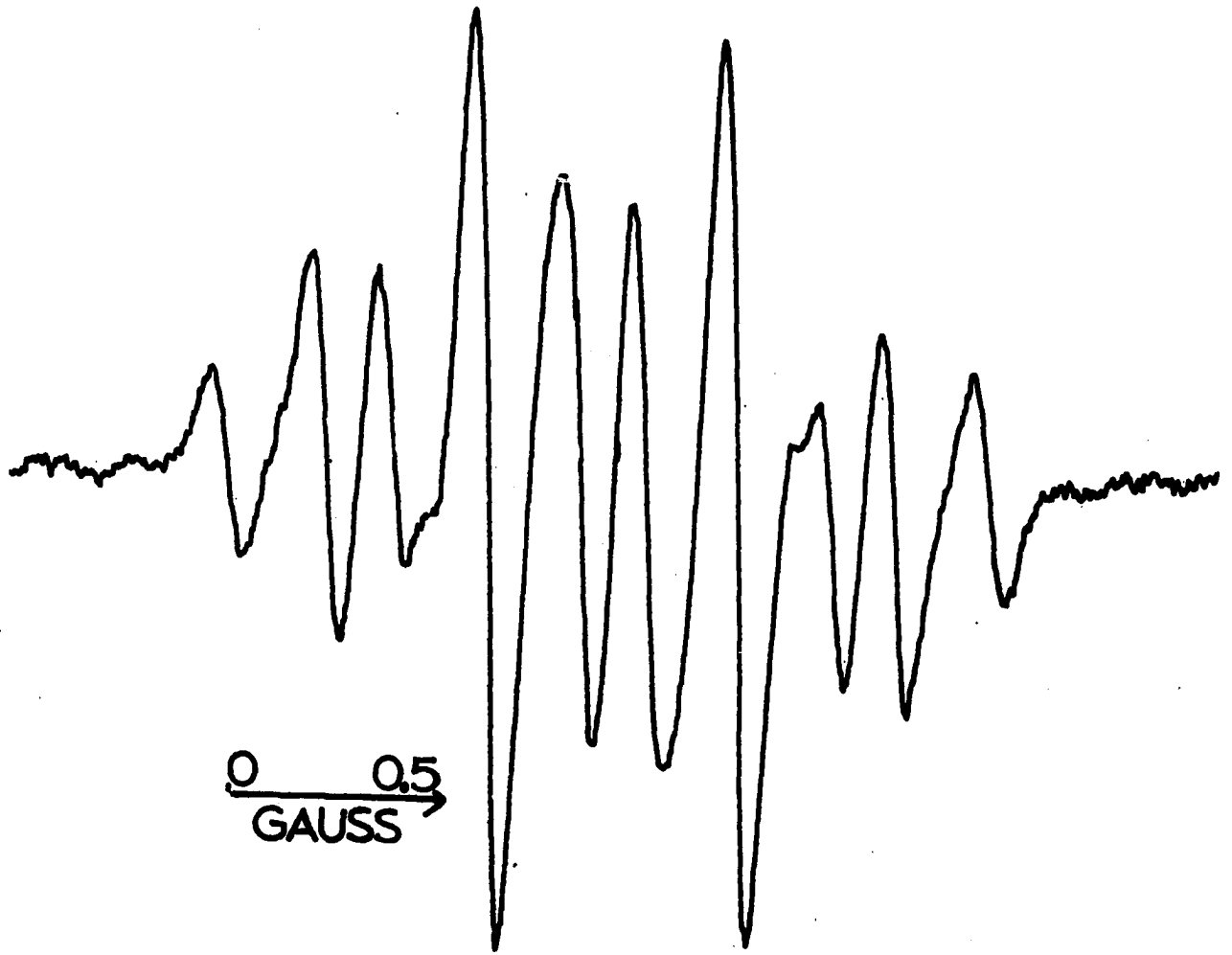


Figure 10. Expansion of a center line in the first-  
derivative ESR spectrum of cyclopropyl methyl  
semidione (top) in DMSO; calculated spectrum  
(bottom) for Lorentzian linewidth of 0.2 gauss  
and splitting constants from text performed  
by JEOLCO JNM-RA-1 spectrum accumulator.

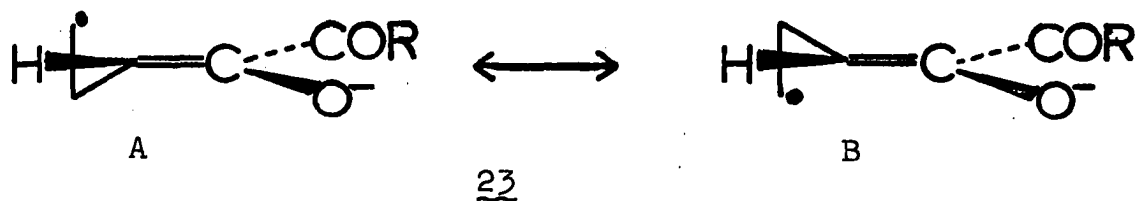




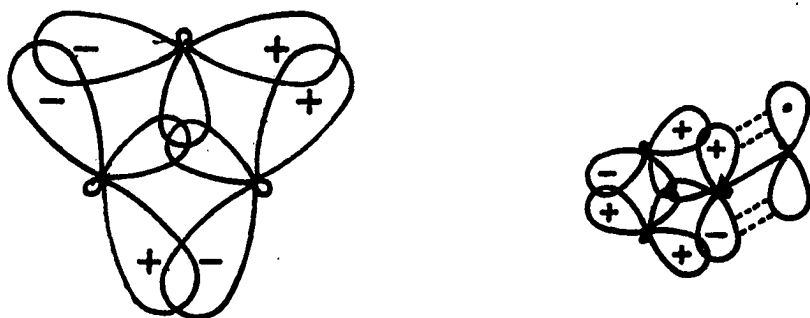
respectively. The small splitting of the  $\alpha$  methine hydrogen atom must result from a highly preferred conformation in which  $H_A$  is close to or in the nodal plane of the  $\pi$  system (diagram 22). The conformation of the cyclopropyl-carbinyl type radical is thus similar to the cyclopropyl carbinyl type cation as in tricyclopropyl carbinyl cation (36). The UV of this cation as well as that of the cyclopropyldimethyl-carbinyl cation displays conjugation of the three membered ring with the  $\pi$  system (37, 38). The 2 to 3 ppm downfield shift of the  $\beta$  proton signal of the cyclopropyl ring has also been attributed to delocalization of the positive charge over all carbon atoms (37, 39, 40). The same conformational preference has been assigned to cyclopropylcarboxaldehyde (41), phenylcyclopropane (42), and various vinyl cyclopropanes (43-45).

Evidence for extensive delocalization in dicyclopropyl semidione lies in the unusual stability of the radical and its high yield. The radical was generated in greater than 50% yield from the acyloin as compared with a diphenylpicrylhydrazyl standard and was stable for days. This unusual stability may be connected with delocalized structures such as A and B in diagram 23 (46).

Structures 23A and 23B are valence bond representations of overlap between the carbinyl system and Walsh (47) or Coulson (48) orbitals on the cyclopropane ring. Walsh formulated the cyclopropane ring as comprising three trigonal

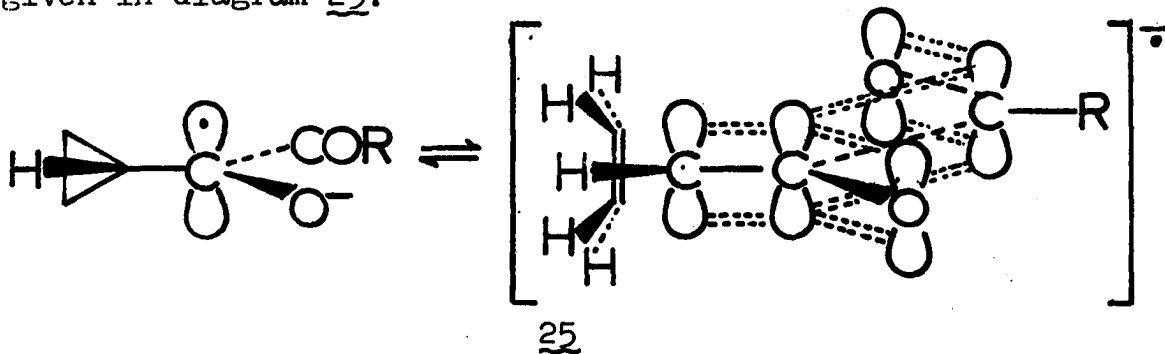


$sp^2$ -hybridized carbon atoms with 2p orbitals situated parallel to each other in one plane. Coulson and Moffit applied the principle of maximum overlap to cyclopropane and proposed  $sp^3$  type bonding orbitals with bond angles between  $102^\circ$  and  $104^\circ$ . The Walsh cyclopropane is shown in diagram 24 along with the delocalized cyclopropylcarbinyl radical (49).



24

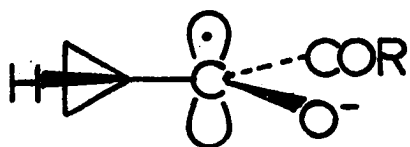
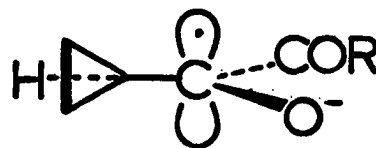
A partial valence bond picture for this delocalization is given in diagram 25.



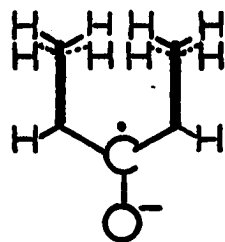
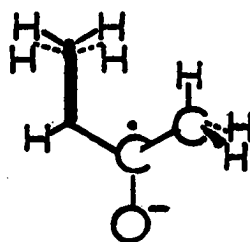
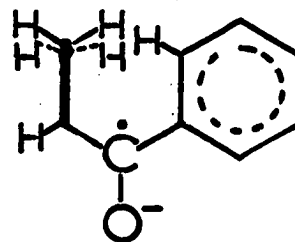
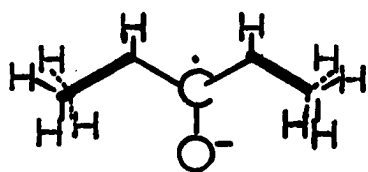
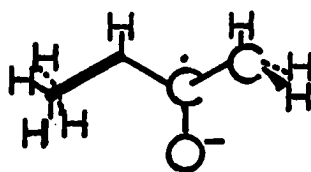
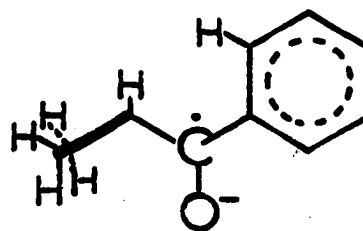
Delocalized cyclopropylcarbiny radicals have been postulated as intermediates (50, 51) in the rearrangement of allylcarbiny radicals and are believed to undergo rapid reversible equilibrium (52) to structures such as 23A and 23B.

Cyclopropane rings have been shown to function as weak proton acceptors in inter- and intramolecular hydrogen bonding (53). This property has been explained in terms of the Coulson-Moffit and Walsh pictures of cyclopropane which portray the three membered ring as a hybrid unsaturated  $\pi$  electron system. The role as a weak Lewis base might explain the rather poor yields of dicyclopropyl acyloin from the acyloin condensation of ethyl cyclopropane carboxylate in ether. Yields less than 1% were obtained as compared with typical yields of 10% and 45% for dicyclopentyl and dicyclohexyl acyloin, respectively. One of the major problems with the reaction is the insolubility of products in ether (54). Coordination between cyclopropane rings and sodium cations could increase the amount of insoluble material and, in effect poison the surface of the sodium sand.

The observed hfsc for the  $\alpha$  methine hydrogen atom can be explained in terms of a single conformer or a time-averaged pair of enantiomeric conformers. The degree of preference will be discussed in the next section. A pair of possible conformers are represented in diagram 26.

AB26

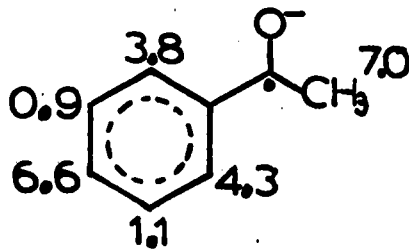
To distinguish between conformers A and B, an experiment was devised in which the steric hindrances would favor one conformation. It was felt that dicyclopropyl ketyl, cyclopropyl methyl ketyl, and cyclopropyl phenyl ketyl would provide good model systems.

27A28A29A27B28B29B

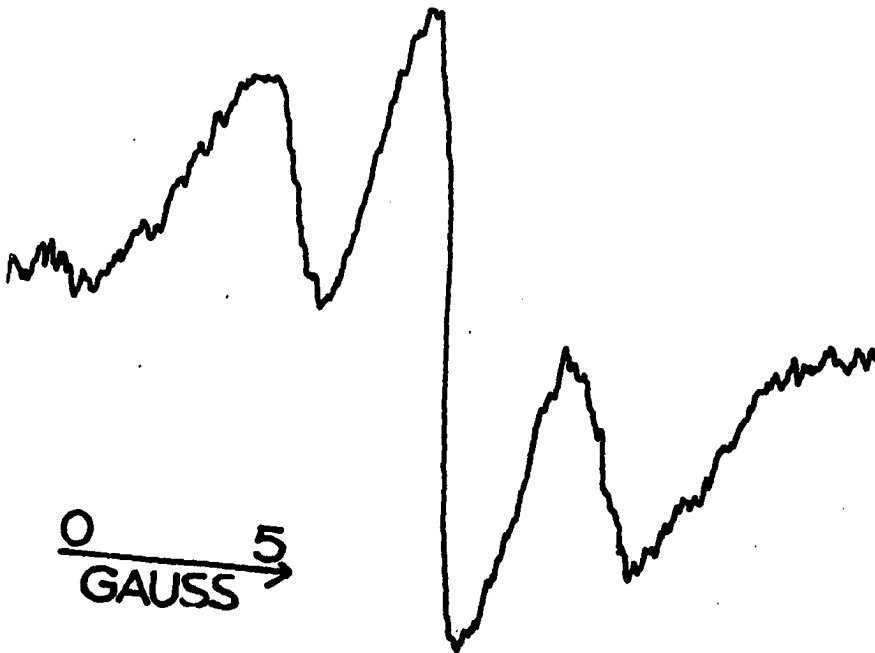
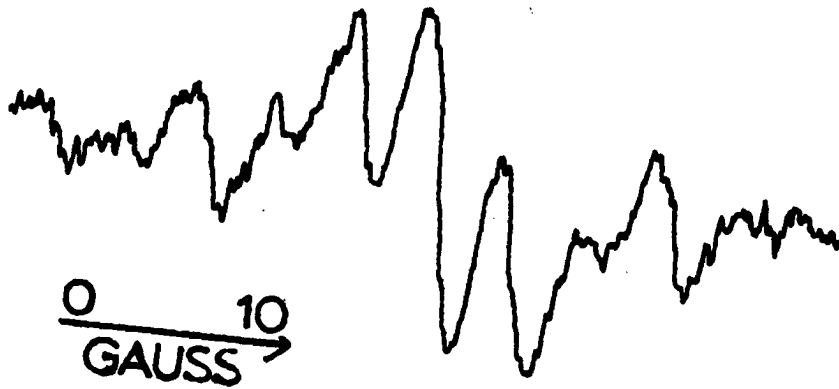
An a priori analysis of the ketyls of the above ketones would yield the following expectations: Conformations 27A and 29A would be sterically unfavorable due to severe proton-proton interactions. If conformation A was required by electronic effects for maximum ring delocalization, then ketyls 27 and 29 probably would not be very stable, and the  $\alpha$  methine hydrogen atom splitting of the cyclopropane ring would be large. Ketyl 28 would not be expected to be stable unless there is unusual stabilization by the cyclopropyl ring. If conformation B is preferred, ketyls 27 and 29 would have a stability approaching that of benzophenone ketyl.

All ESR signals from 0.1 N ketone solutions in dimethoxy-methane (DME) and potassium metal were weak. Cyclopropyl methyl ketyl gave an unresolvable signal which disappeared after ten minutes (Figure 11a). Cyclopropyl phenyl ketyl displayed a weak ESR singlet which was split into five lines, a doublet of 5.8 gauss and a triplet of 3.9 gauss (Figure 11b). The spectrum is similar in appearance to that of acetophenone ketyl (55).

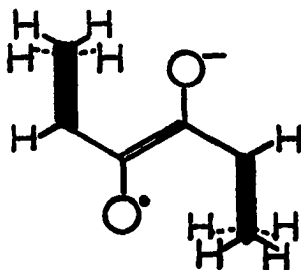
Acetophenone ketyl has the following splitting constants (56):



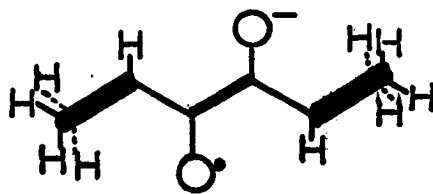
- Figure 11. (a) First-derivative ESR spectrum of cyclopropyl methyl ketyl (top) generated by reduction of the ketone with potassium in DME.
- (b) First-derivative ESR spectrum of cyclopropyl phenyl ketyl (middle) generated by reduction of the ketone with potassium in DME.
- (c) First-derivative ESR spectrum of dicyclopropyl ketyl (bottom) generated by reduction of the ketone with potassium in DME.



If the 5.8 gauss doublet is assigned to the para position of the cyclopropyl phenyl ketyl, and the 3.9 gauss triplet is assigned to the meta hydrogens, then the splitting constant of the  $\alpha$  methine hydrogen atom will be less than 2 gauss. However, the ketyl is unstable, and the signal disappears after thirty minutes. Dicyclopropyl ketyl (Figure 11c) gives the strongest signal of the series, a triplet of 3.5 gauss (46, 55, 57). The signal is still poorly resolved but has a half-life of more than 30 minutes. When this hfsc is compared with the  $\alpha$  methine hydrogen splitting of 2.38 gauss for the ketyl (58) of  $(\text{CH}_3)_2\text{CH-CO-C}(\text{CH}_3)_3$  and 2.1 gauss for the ketyl (59) of  $(\text{C}_2\text{H}_5)_2\text{CH-CO-C}(\text{CH}_3)_3$ , the conclusion is that there is only a small conformation preference. This will be discussed quantitatively in the next section. Thus, it appears that conformation A is favored in the ketyl system. Similar structures for the semidione system are shown in diagram 31. The three-membered rings are shown end on and are represented



A Cisoid conformer



B Transoid conformer



by a thick black line. The cyclopropyl ring in conformation A is cis with respect to the carbon-carbon bond in the semidione system and is thus referred to as cisoid. Similarly, conformation B is referred to as the transoid conformer.

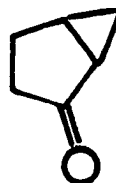
The semidione system is ideal in respect to stability of derivatives. The semidione of acetoin or dimethyl semidione (60) is stable for days, and even the parent glyoxal radical anion (16, 61) has been prepared. In the trans semidione structure such as 31A or 31B there is little or no communication between substituents. For example, in the series cyclopropyl methyl, cyclobutyl methyl, cyclopentyl methyl, cyclohexyl methyl, and cyclooctyl methyl, the methyl splittings (5.88 gauss, 5.55 gauss, 5.77 gauss, 5.73 gauss, and 5.85 gauss, respectively) vary little and do not seem to reflect any specific steric or electronic effect. Dimethyl semidione generated at room temperature with potassium t-butoxide in DMSO exists as a mixture of 5% cis and 95% trans isomers (62). Molecular Framework Models (Prentice-Hall, Inc., Englewood Cliffs, N. J.) of dimethyl semidione and cyclopropyl methyl semidione demonstrate a lack of steric repulsion in the cis configuration of the two, provided that the latter is in the B or transoid conformation. In the A or cisoid conformation, there is considerable 6-bond interaction between the cyclopropane ring and the methyl group. Therefore, the experimental lack of cis isomer, either in potassium t-butoxide or sodium t-butoxide - DMSO solution, is consistent with the cisoid

conformation.

The author favors cisoid delocalization in dicyclopropyl semidiones on the basis of the large  $\alpha$  hydrogen atom splitting constant in dicyclopropyl ketyl and the experimental lack of cis isomer formation in methyl cyclopropyl semidione. However, there is little evidence in other systems requiring either cisoid or transoid three-membered rings for maximum stabilization. Electron diffraction studies of Bartell (41) indicate a 50-50 mixture of cis and trans forms in cyclopropanecarboxaldehyde. Ketones 32 and 33 exhibit similar UV absorption maxima ,

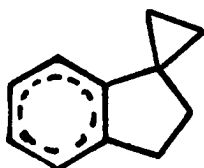


32

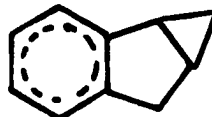


33

and those of 34 and 35 are nearly identical (63, 64).



34



35

Jorgensen and Leung (45) claimed the UV studies of cyclopropylacrylic esters showed a clear preference for a trans ring conformation. At the same time Heathcock and Poulter (44) found no preference between the two conformers in cyclopropyl olefins.

One factor which is expected to affect the stability of cisoid ring conjugation is substitution on the cyclopropane ring. A 1-methyl substituent would not be expected to affect the population of either conformation. 1-(1-Methylcyclopropyl)-2-propanone was prepared according to the literature (65) and was oxidized with oxygen in potassium t-butoxide-DMSO solution. The resulting ESR spectrum was poorly resolved and yielded no definite assignments. Methyl substitution in the methylene position of the cyclopropane ring is expected to have a marked effect on the stability of cisoid cyclopropane semidione. A tetramethylcyclopropane ring is expected to populate the linear conformation exclusively. Ethyl 2,2,3,3-tetramethylcyclopropane carboxylate was prepared from the 2,3-dimethyl-2-butene and ethyl diazoacetate. The ester, however, failed to undergo the acyloin condensation either in sodium sand and refluxing ether or in sodium and hot (105-110°) xylene. This lack of reactivity might be due to unusual steric crowding required in the cis transition state (66). A 2,2-dimethylcyclopropane ring is expected to greatly hinder conjugation. 1-(2,2-Dimethylcyclopropyl)-2-propanone

and 1-(2,2-dimethylcyclopropyl)-1-propanone were prepared via a Simmons-Smith reaction (67) on the ethylene ketals of the corresponding ketones. The former ketone failed upon oxidation to produce a radical anion, and the latter displayed only a poorly resolved spectrum. Finally, ethyl 2,2-dimethylcyclopropane carboxylate was synthesized. The ester was converted via the acyloin condensation to di-2,2-dimethylcyclopropyl acyloin. The ESR signal of the corresponding semidione consisted of a large 1:2:1 triplet of at least 41 lines (Figure 12). The spectrum was analyzed by synthesizing 2,2-dimethylcyclopropyl methyl acyloin. The radical anion of this compound displayed a quartet splitting of 5.79 gauss, a doublet of 1.49 gauss, a doublet of 0.65 gauss, a quartet of 0.27 gauss, and a doublet of 0.09 gauss (Figures 13, 14). The large quartet is caused by the methyl semidione hydrogens and the small quartet by the methyl group ( $H_D$ ) cis to the  $\alpha$  methine hydrogen atom ( $H_A$ ).

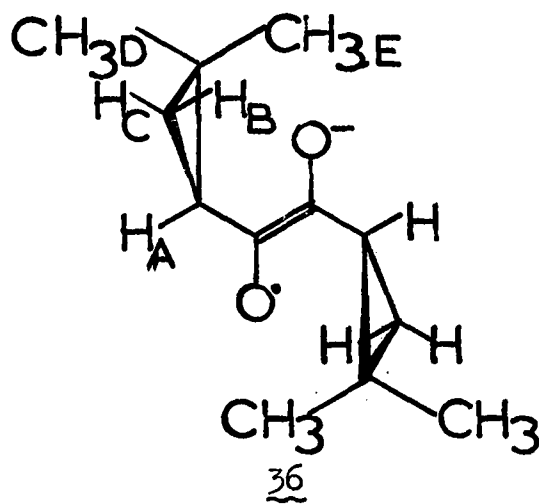


Figure 12. First-derivative ESR spectrum of di-2,2-dimethyl-cyclopropyl semidione (top) in DMSO; calculated spectrum (bottom) for Lorentzian linewidth of 0.2 gauss and splitting constants from text performed by JEOLCO JNM-RA-1 spectrum accumulator.

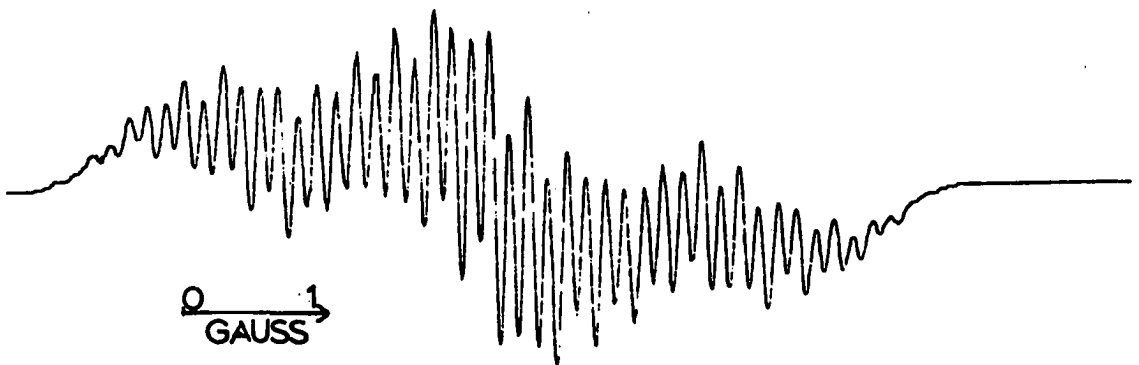
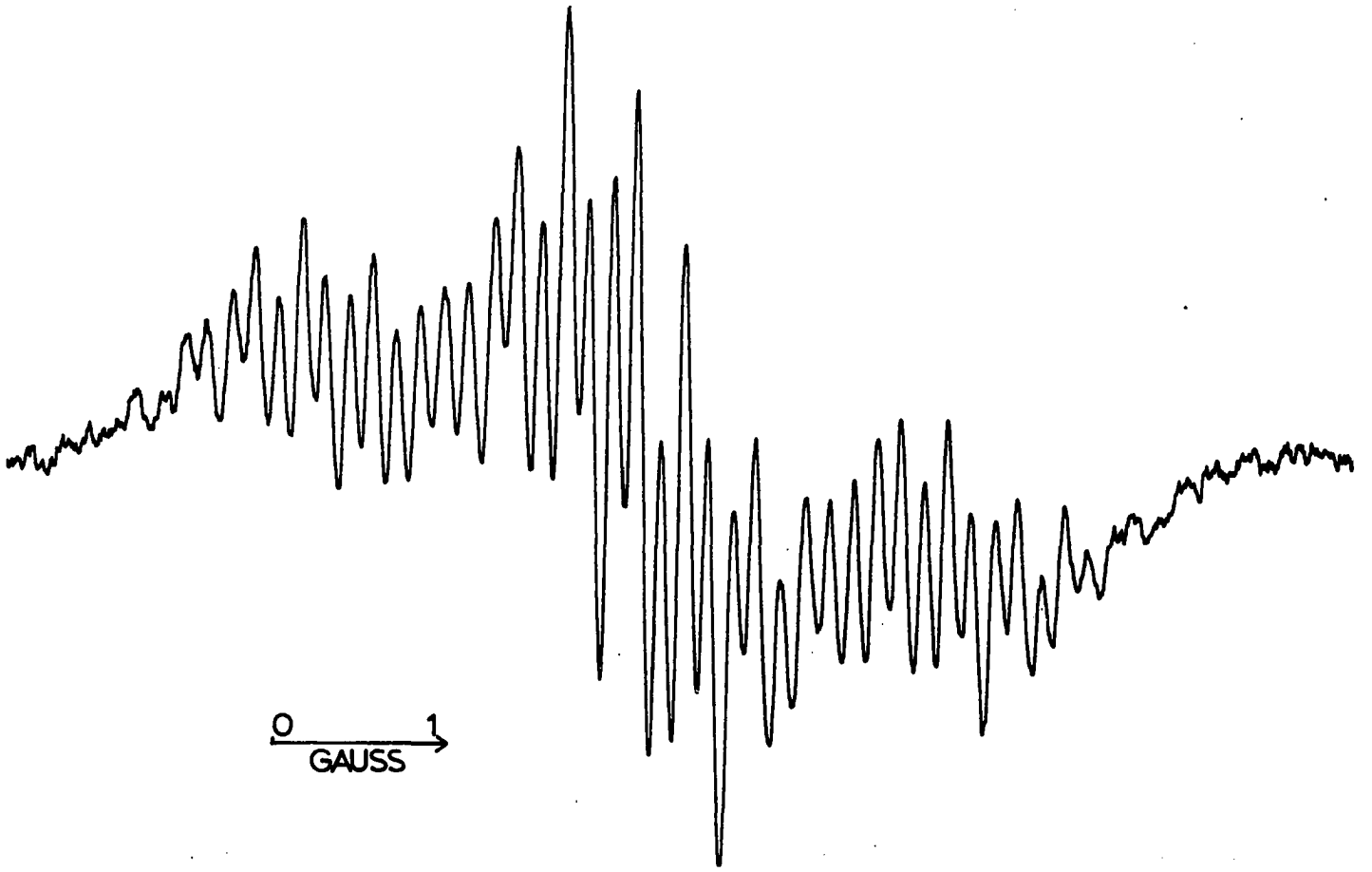


Figure 13. First-derivative ESR spectrum of 2,2-dimethyl-cyclopropyl methyl semidione in DMSO.

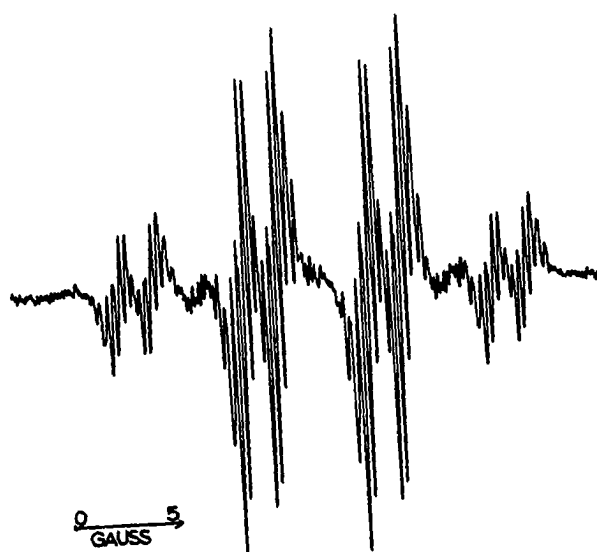
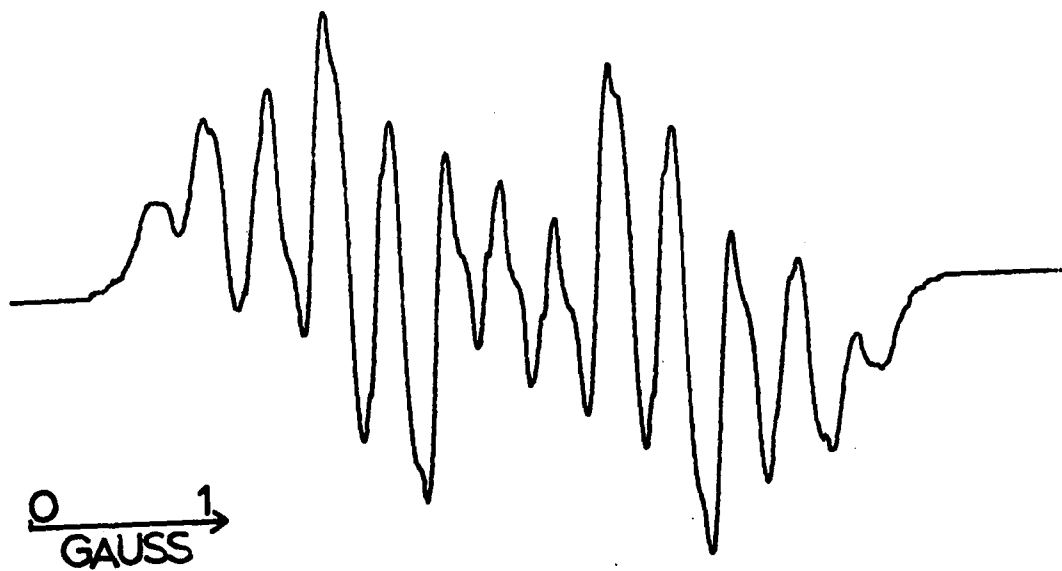
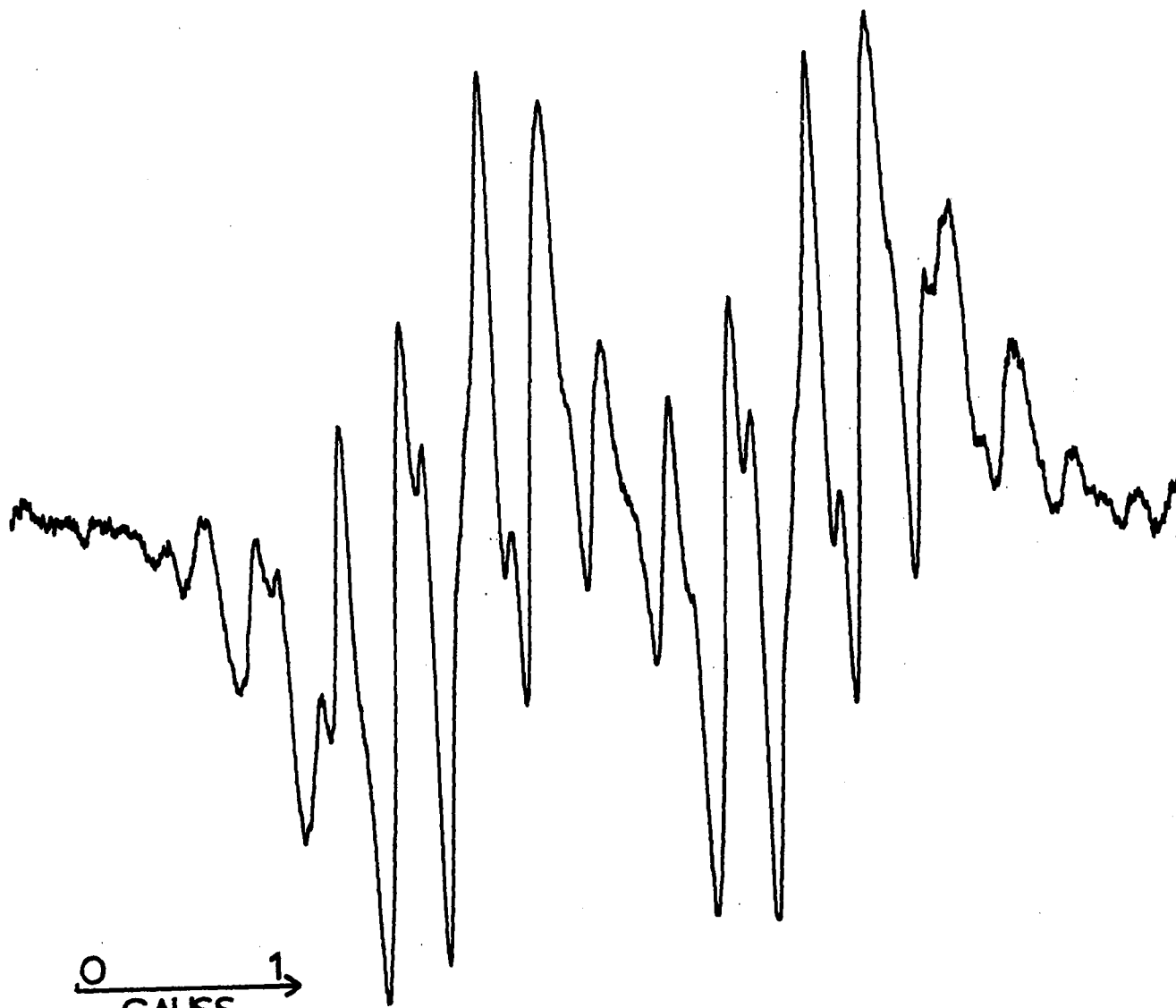




Figure 14. Expansion of a center line in the first-derivative ESR spectrum of 2,2-dimethylcyclopropyl methyl semidione (top) in DMSO; calculated spectrum (bottom) for Lorentzian linewidth of 0.2 gauss and splitting constants from text performed by JEOLCO JNM-RA-1 spectrum accumulator.

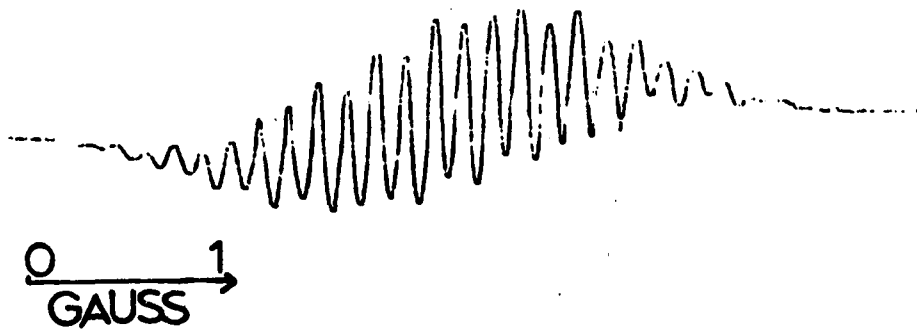
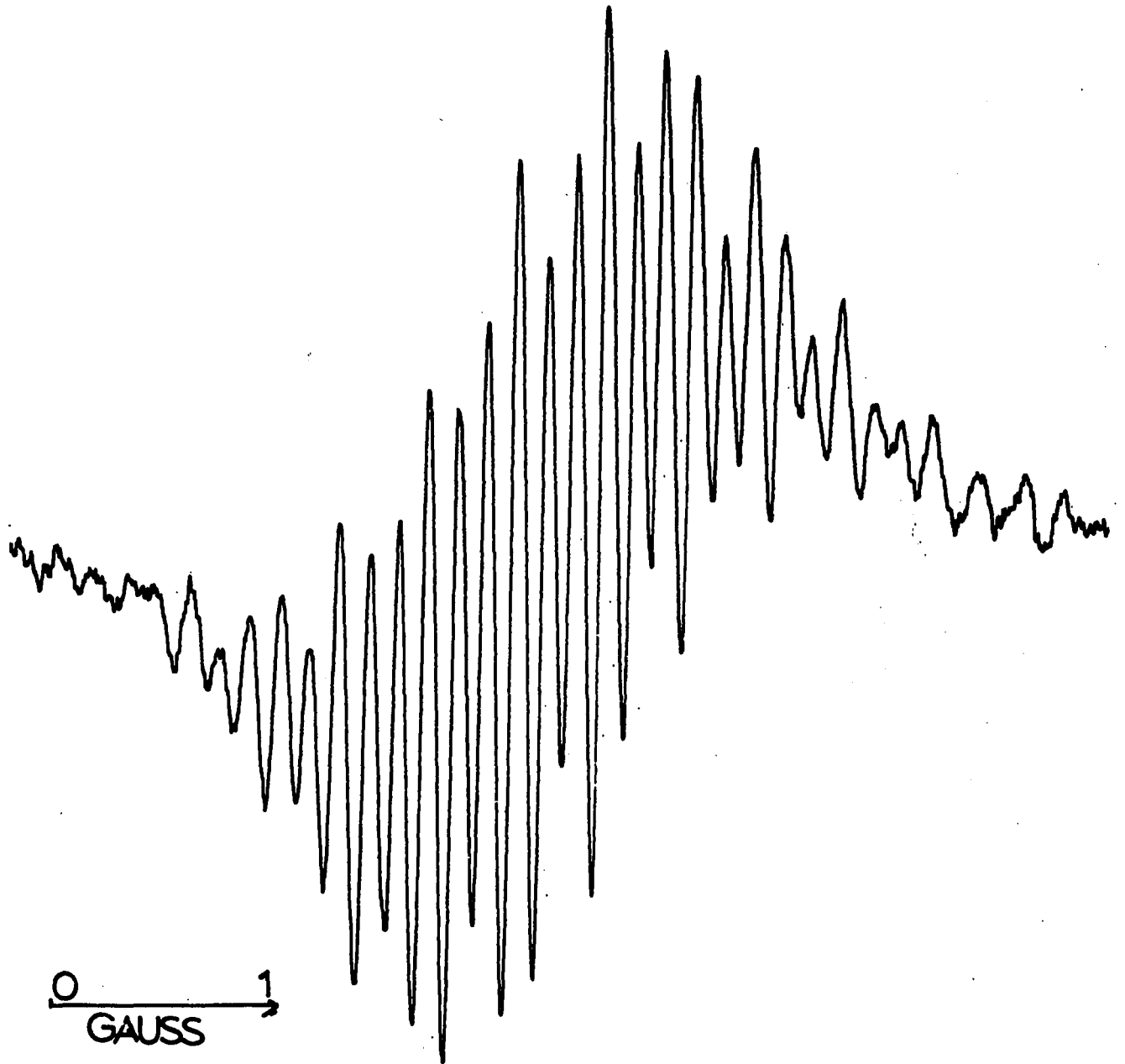


The 1.49 gauss doublet is assigned to the  $\alpha$  methine hydrogen atom ( $H_A$ ), the 0.65 doublet to the ring hydrogen ( $H_C$ ) cis to  $H_A$ , and the 0.08 doublet to the ring hydrogen ( $H_B$ ) trans to  $H_A$  (diagram 36). These assignments are based upon the double-V plan interaction. It is believed that this interaction is more important than direct overlap between the p orbitals on oxygen and either  $H_B$  or  $CH_3(E)$ . Thus, the 0.26 gauss quartet was assigned to  $H_D$  rather than to  $H_E$ . There still remains some ambiguity in assigning  $H_A$ . This was solved by generating bis-2,2-dimethylcyclopropane semidione in  $d_6$ -DMSO. The corresponding hfsc for bis-2,2-dimethylcyclopropyl semidione are 1.49, 0.65, 0.27, and 0.10 gauss assigned to  $H_A$ ,  $H_C$ ,  $H_D$ , and  $H_B$ , respectively. The radical anion exchanged slowly and after 24 hours displayed a narrow spectrum of 30 or more lines (Figure 15). The spectrum was synthesized using a  $\alpha$  methine deuterium splitting constant of 0.24 gauss. This represents a  $a^H/a^D$  equal to 6.2 and is consistent with a normal ratio of 6.5 (68).

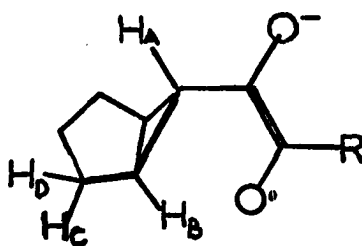
Thus we see that methyl substituents on the cyclopropane ring alter the conformation and cause the  $\alpha$  methine hydrogen atom to twist slightly out of the nodal plane of the  $\Pi$  system. This finding is consistent with either the cisoid or transoid conformers.

Symmetric substitution of the cyclopropane ring was accomplished through the synthesis of fused three-membered

Figure 15. First-derivative ESR spectrum of di-2,2-dimethylcyclopropyl semidione (top) in DMSO-d<sub>6</sub> after two days; calculated spectrum (bottom) for Lorentzian linewidth of 0.2 gauss and splitting constants from text performed by JEOLCO JNM-RA-1 spectrum accumulator.



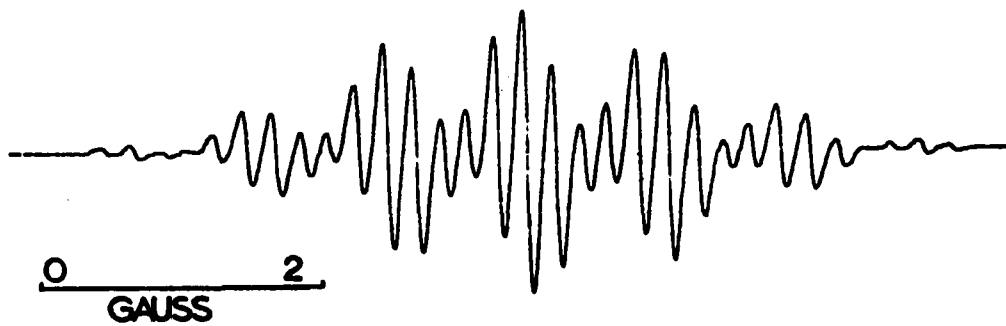
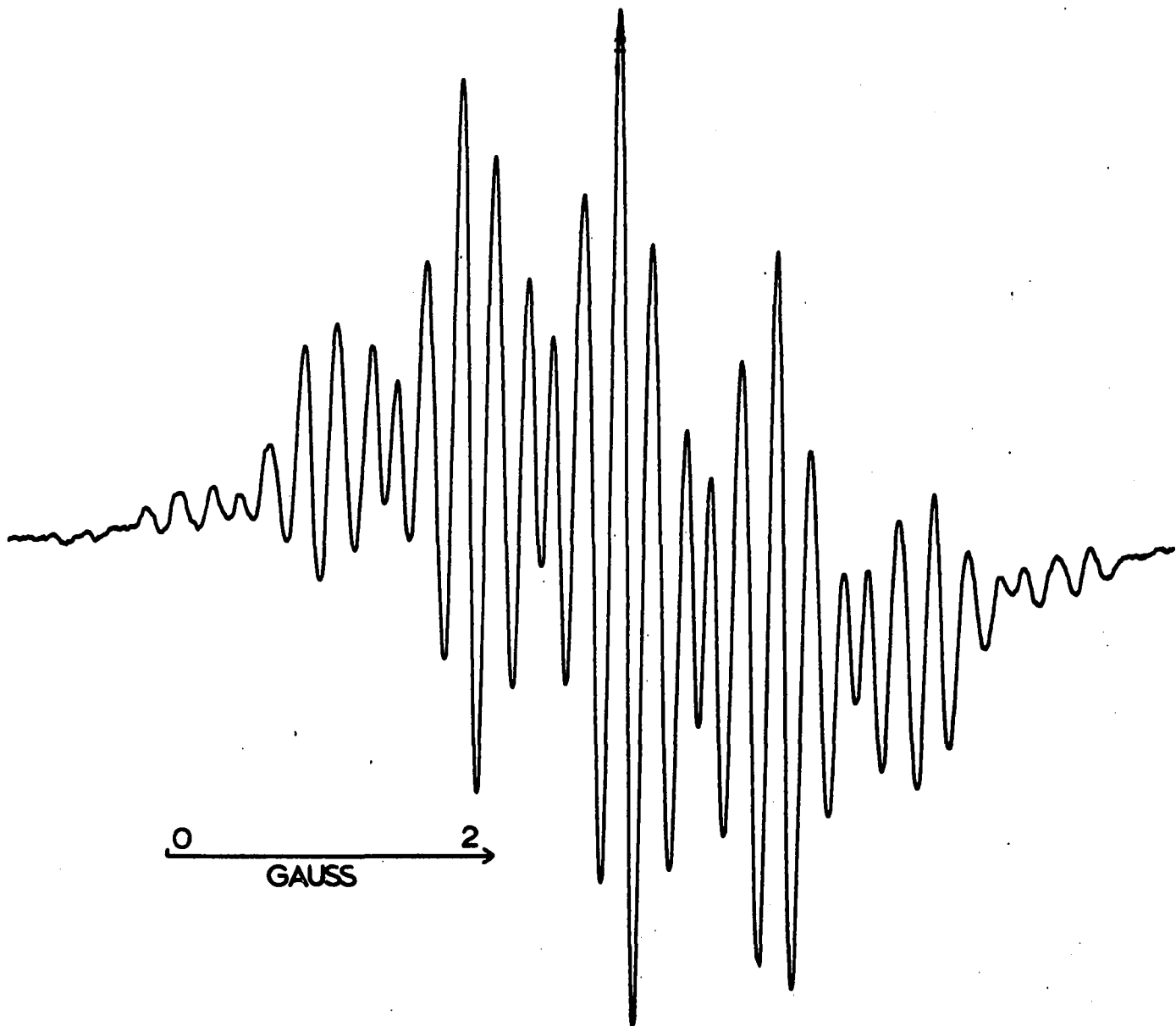
ring compounds. The first of the series, di-6-bicyclo-[3.1.0]hexyl acyloin, upon conversion to the semidione, yielded a basic pentet of triplets (Figure 16). The triplet hfsc of 0.75 gauss is assigned to the  $\alpha$  methine hydrogen atoms ( $H_A$ ). The small magnitude of this splitting is an indication of either conformer 31A or 31B. The cisoid conformation is shown in diagram 37. The large pentet splitting of 0.95 gauss



37

is assigned the  $\beta$  cyclopentane ring hydrogens ( $H_C$ ) trans to the cyclopropane ring. This assertion is based on the rather good two and a half V plan arrangement between  $H_C$  and the  $\pi$  orbital on the carbonyl carbon and on the fact that the C- $H_C$  bond is parallel and anti to the plane of the cyclopropane ring. This last arrangement appears to be most favorable for cyclopropyl ring conjugation (69). The remaining splitting, a small pentet of 0.20 gauss, is assigned to the remaining cyclopropyl hydrogens ( $H_B$ ). This assignment is based on semidiones already discussed. The  $H_B$  hydrogen atoms in dicyclopropyl semidione and bis-2,2-dimethylcyclopropyl semidione have hfsc

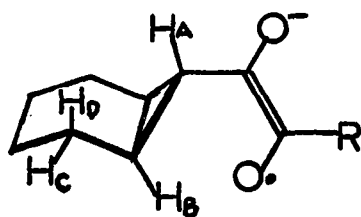
Figure 16. First-derivative ESR spectrum at di-6-bicyclo[3.1.0]hexyl semidione (top) in DMSO; calculated spectrum (bottom) for Lorentzian linewidth of 0.2 gauss and splitting constants from text performed by JEOLCO JNM-RA-1 spectrum accumulator.





of 0.19 and 0.10, respectively. The C-H<sub>B</sub> bond is perpendicular to the plane of the cyclopropyl carbon atoms, i.e., parallel to the nodal plane of the  $\pi$  system. Consequently, a weak interaction is expected.

The semidione of di-7-bicyclo[4.1.0]heptyl acyloin gave a symmetrical ESR spectrum of 24 equally spaced lines (Figure 17). 7-Bicyclo[4.1.0]heptyl methyl acyloin was synthesized to aid in the interpretation of this spectrum (Figures 18 and 19). The semidione of the mixed acyloin displayed an ESR signal



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consistent with the following hfsc: a 6.00 gauss quartet, three triplets of 0.78 gauss, 0.48 gauss, and 0.27 gauss, and a 0.52 gauss doublet. The quartet splitting is due to the semidione methyl group. The doublet of 0.52 gauss is assigned to the  $\alpha$  methine hydrogen atom (H<sub>A</sub>, diagram 38) and is indicative of a highly preferred conformation. The 0.27 gauss triplet is caused by the remaining cyclopropane ring hydrogens (H<sub>B</sub>). The increased ring size distorts the two and a half V

Figure 17. First-derivative ESR spectrum of di-7-bicyclo[4.1.0]heptyl acyloin in DMSO.

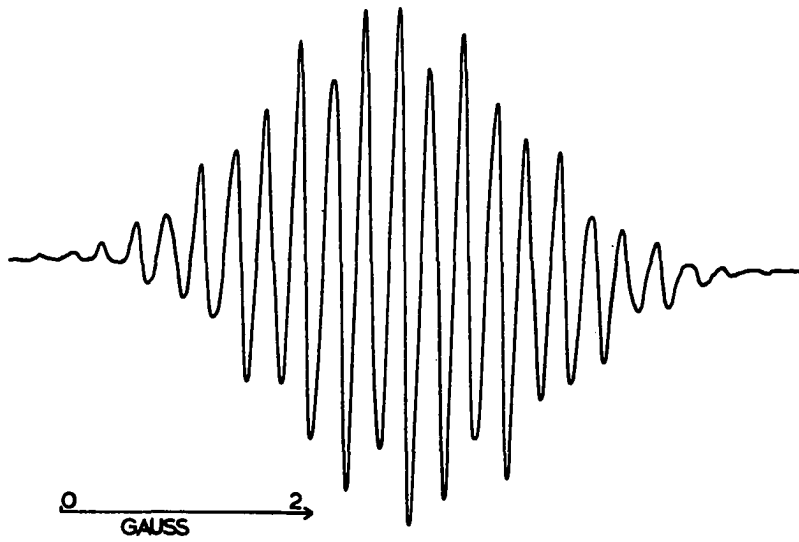


Figure 18. First-derivative ESR spectrum of 7-bicyclo-  
[4.1.0]heptyl methyl semidione in DMSO.

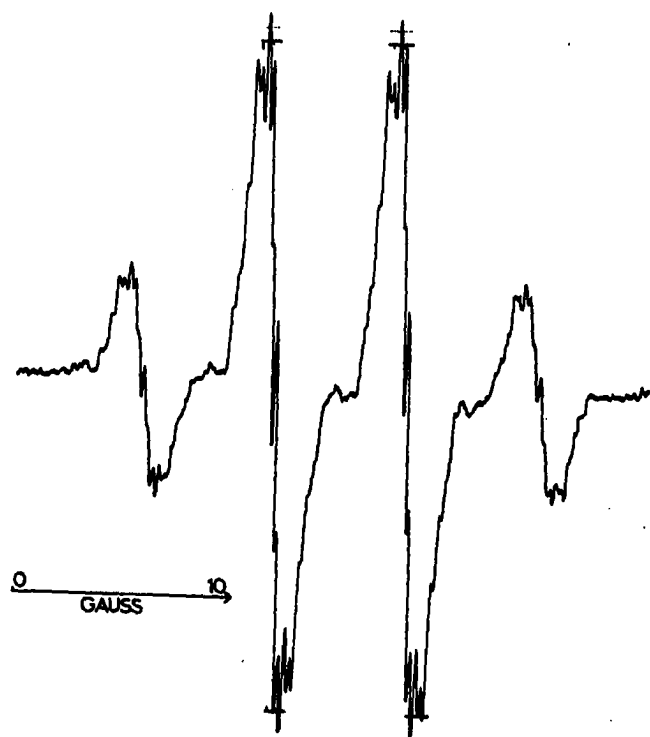
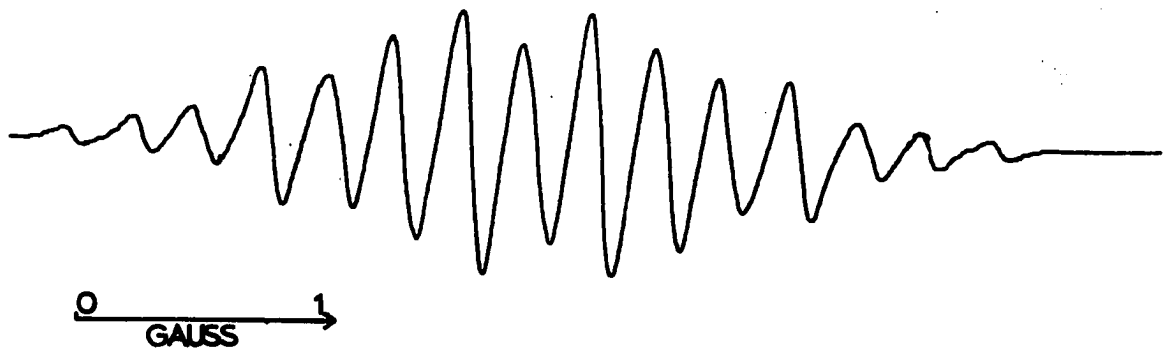
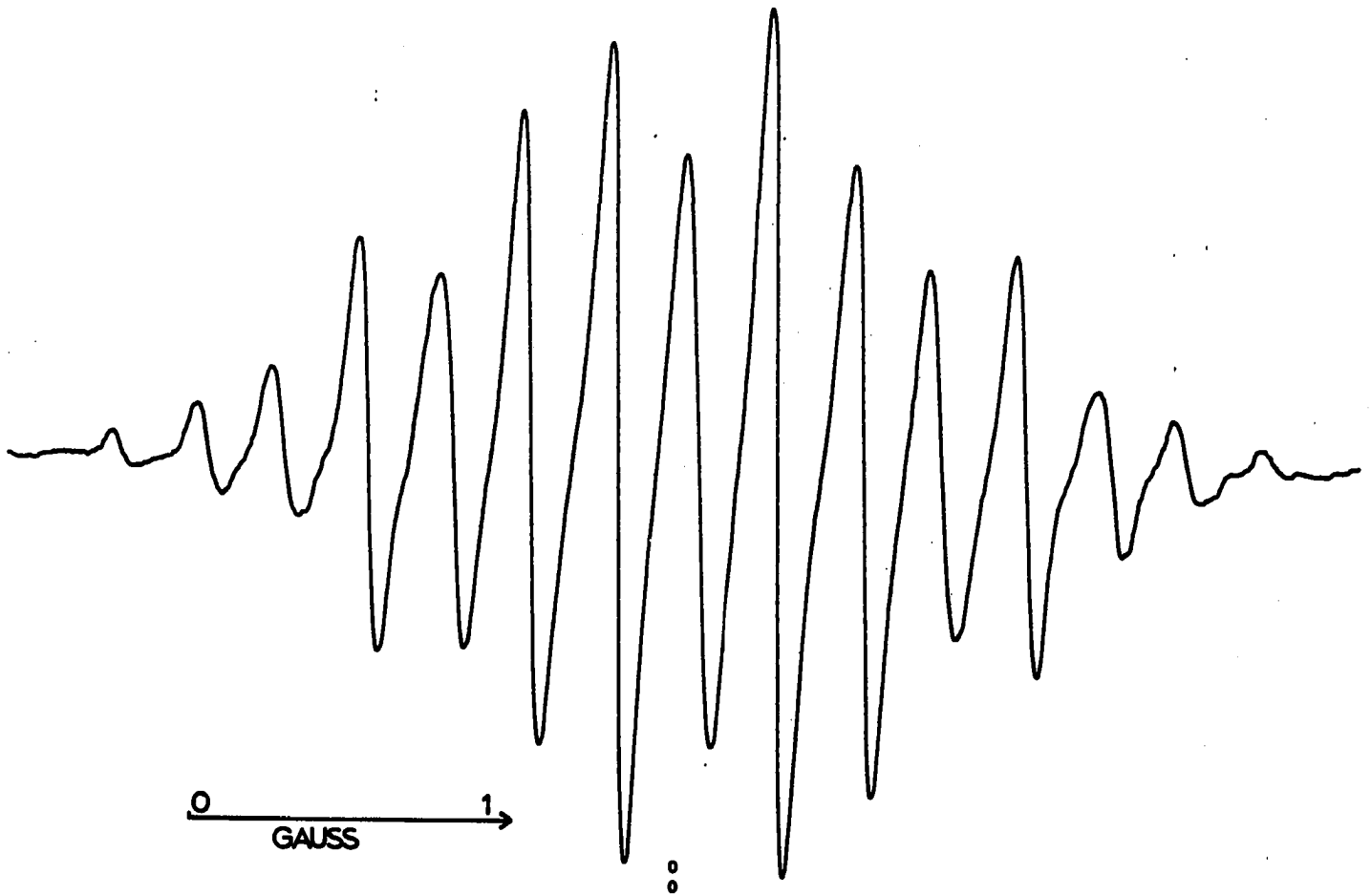


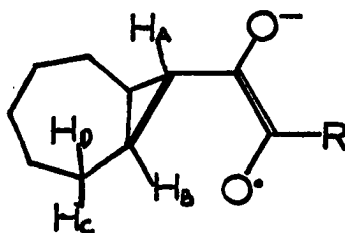
Figure 19. Expansion of a center line in the first-  
derivative ESR spectrum of 7-bicyclo[4.1.0]-  
heptyl methyl semidione (top) in DMSO;  
calculated spectrum (bottom) for Lorentzian  
linewidth of 0.2 gauss and splitting constants  
from text performed by JEOLCO JNM-RA-1 spectrum  
accumulator.



plan arrangement between the carbinyl  $\pi$  orbital and the cyclohexane ring hydrogen  $H_C$  and lowers the hfsc from 0.95 in rigid di-6-bicyclo[3.1.0]hexyl acyloin to 0.78 gauss. This distortion (70, 71) similarly increases the splitting constants of  $H_D$ . These hydrogen atoms are not observed in the [3.1.0] system and assume a hfsc of 0.48 gauss.

The corresponding hfsc for di-7-bicyclo[4.1.0]heptyl semidione are 0.78 gauss (4H), 0.52 gauss (2H), 0.48 gauss (4H), and 0.27 gauss (4H) for hydrogen atoms  $H_C$ ,  $H_A$ ,  $H_D$ , and  $H_B$ , respectively.

The semidione of di-8-bicyclo[5.1.0]octyl acyloin displayed a complex spectrum (Figure 20) which was simulated with reference to the spectra of the two previous members of the series. The spectrum consisted of a triplet of 0.48 gauss, a nonet of 0.37 gauss, and a pentet of 0.13 gauss.

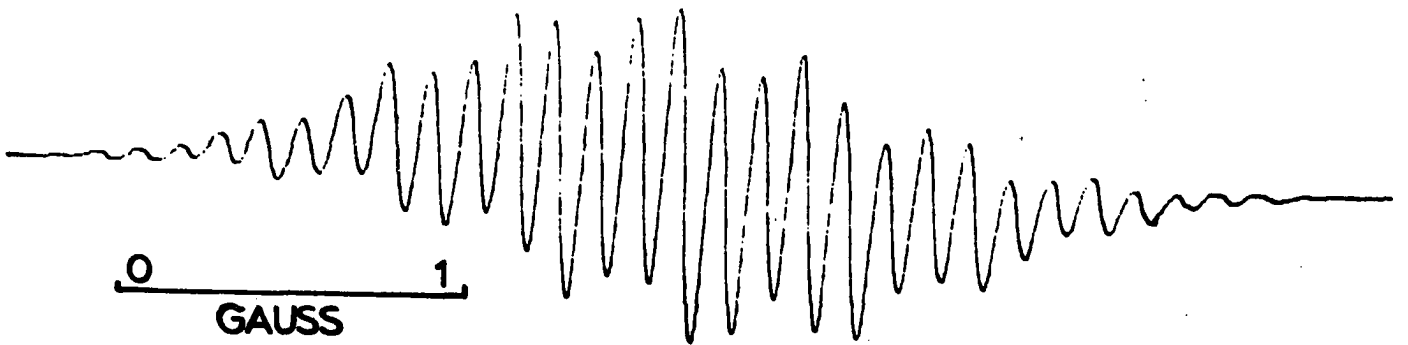
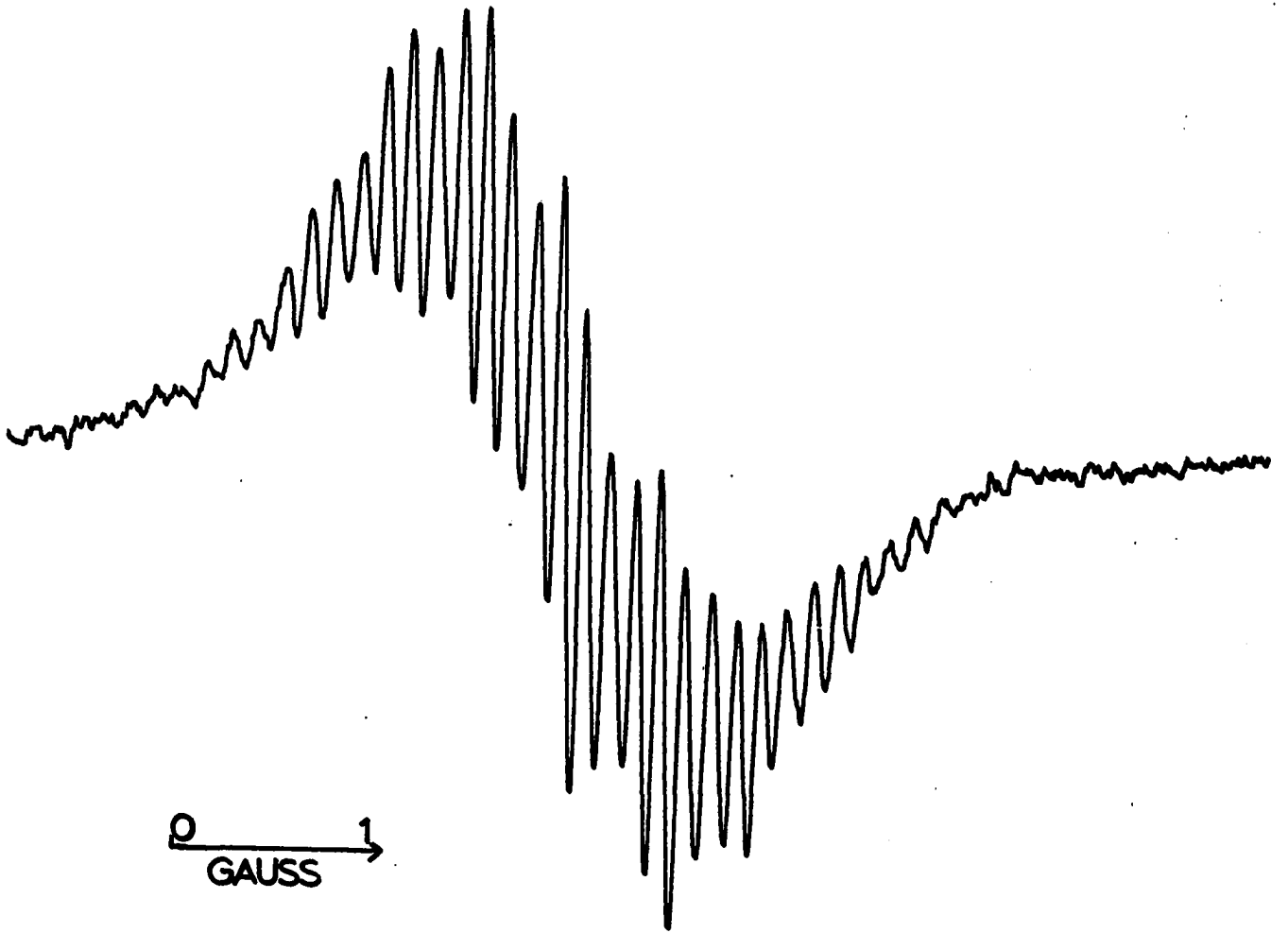


### 39

The triplet is due to the  $\alpha$  methine hydrogen atom ( $H_A$ , diagram 39). This, as in the previous members of the series, is indicative of a highly preferred conformation. The nonet of



Figure 20. First-derivative ESR spectrum of di-8-bicyclo[5.1.0]octyl acyloin (top) in DMSO; calculated spectrum (bottom) for Lorentzian linewidth of 0.2 gauss and splitting constants from text performed by JEOLCO JNM-RA-1 spectrum accumulator.



0.37 gauss is assigned to the  $\beta$  cycloheptane ring hydrogens ( $H_C$ ,  $H_D$ ). The small magnitudes of the hfsc of  $H_C$  and  $H_D$  and their apparent equivalence reflect either rapid interconversion of the fused cycloheptane ring (30) or, more likely, fortuitous splitting caused by the increased distortion of the two and a half V interaction. This interaction becomes progressively unfavorable in the series di-6-bicyclo[3.1.0]hexyl, di-7-bicyclo[4.1.0]heptyl, di-8-bicyclo[5.1.0]octyl, and di-8-bicyclo[6.1.0]nonyl semidiones. The pentet of 0.13 gauss is assigned the remaining cyclopropane ring hydrogens ( $H_B$ ). An alternative assignment places the 0.13 gauss splitting on  $H_D$  and the 0.37 gauss splitting on  $H_B$  and  $H_C$ .

The last member of the fused three-membered ring series, di-9-bicyclo[6.1.0]nonyl semidione, gave a poorly resolved signal (Figure 21). The experimental line width of the spectrum was 3.30 gauss as compared with 4.50 gauss for di-8-bicyclo[5.1.0]octyl semidione, 7.20 gauss for di-7-bicyclo[4.1.0]heptyl semidione, and 6.10 gauss for di-6-bicyclo[3.1.0]hexyl semidione. This is indicative of small splitting constants and a preferred conformation.

Tables 2 and 3 summarize the data presented in this section.

Figure 21. First-derivative ESR spectrum of di-9-bicyclo[6.1.0]nonyl semidione in DMSO.

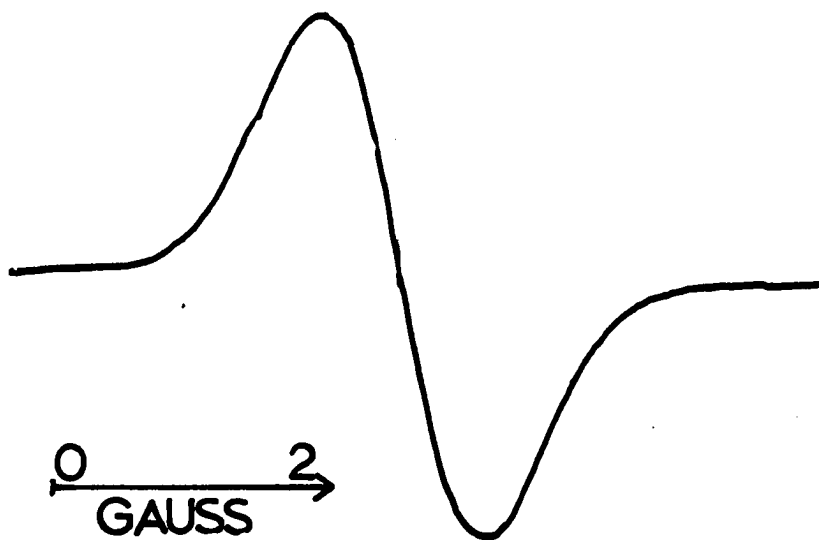
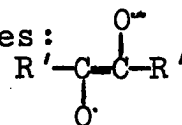


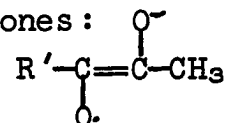
Table 2. Hyperfine splitting constants of semidiones:



R'	$a_\alpha$ (gauss)	$a_\beta$ (gauss)	$a_\gamma$ (gauss)
Cyclobutyl	2.22	0.45 (4H), 0.23 (4H)	0.08 (2H)
Cyclopentyl	1.92	0.44 (4H), 0.22 (4H)	0.11 (4H)
Cyclohexyl	1.88		
Cycloheptyl	1.95		
4-Cycloheptenyl	2.08	0.18 (8H)	
Cyclopropyl	0.57	0.37 (4), 0.19 (4)	
2,2-Dimethylcyclopropyl	1.49	0.65 (2), 0.10 (2)	0.27 (6H)
6-Bicyclo[3.1.0]-hexyl	0.75	0.20 (4)	0.95 (4H)
7-Bicyclo[4.1.0]-heptyl	0.52	0.27 (4)	0.78 (4H), 0.48 (4H)
8-Bicyclo[5.1.0]-octyl	0.48	0.13 (4), 0.37 (8H) <sup>a</sup>	
9-Bicyclo[6.1.0]-nonyl	Total spectrum one line 3.30 gauss wide		

<sup>a</sup>Definitive assignments cannot be made.

Table 3. Hyperfine splitting constants for semidiones:



R'	$a_{\text{CH}_3}$ (gauss)	$a_\gamma$ (gauss)	$a_\beta$ (gauss)	$a_\gamma$ (gauss)
Cyclobutyl	5.55	2.11	0.44(2H), 0.23 (2H)	
Cyclopentyl	5.77	1.92	0.44(2H), 0.22 (2H)	0.11(2H)
Cyclohexyl	5.73	1.73	0.30(4H) <sup>a</sup> , 0.08(4H) <sup>a</sup>	
Cyclooctyl	5.85	1.94	0.09(4H) <sup>a</sup>	
Cyclopropyl	5.88	0.57	0.37(2H), 0.20 (2H)	
2,2-Dimethylcyclopropyl	5.79	1.49	0.65(1H), 0.09 (1H)	0.27(3H)
7-Bicyclo[4.1.0]-heptyl	6.00	0.52	0.27(2H)	0.78(2H), 0.48(2H)

<sup>a</sup>Definitive assignments cannot be made.

The  $\alpha$  Methine Hydrogen Atom

This section is devoted to the interpretation of the  $\alpha$  methine hydrogen atom hfsc. The splitting constant of this hydrogen atom has been explained in terms of conformation (1). The subject is thoroughly reviewed by Geske with emphasis on nitroaromatic radical anions (5). The conformation of semidiones, in particular, steroidal semidiones and cyclic semidiones, has been discussed in a series of papers by Russell *et al.* (16, 18, 72, 73). We will discuss the conformation of dicyclic as well as acyclic semidiones with particular emphasis on steric and electronic factors. The major concern will be the orientation of C-H bonds with respect to the nodal plane of an adjacent semidione  $\pi$  system.

In 1959 Symons suggested that the  $\alpha$  hydrogen atom hfsc would follow a  $\cos^2\theta$  law with respect to the angle between the C-H bond and the axis plane of the  $\pi$  system (1). Heller and McConnell improved upon this relationship and proposed the following relationship:

$$a^H = B_0 + B\cos^2\theta$$

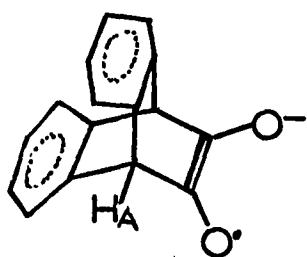
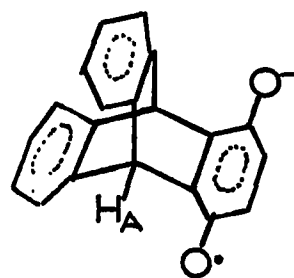
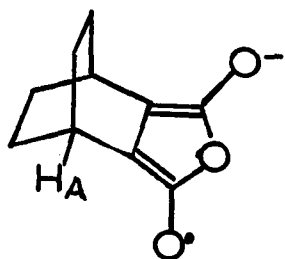
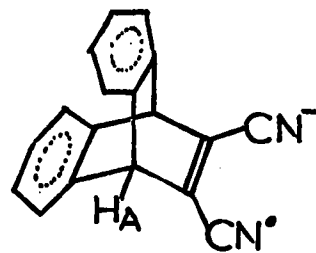
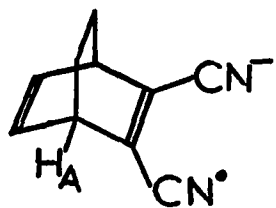
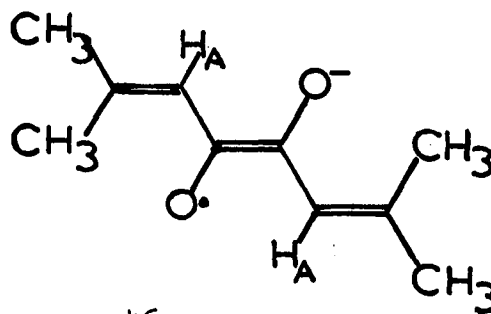
B is a constant between 40 and 60 gauss.  $B_0$ , a small value, is the splitting constant of a hydrogen in the nodal plane, *i.e.*,  $\theta = 90^\circ$  (2). Stone and Maki introduced the concept of a time averaged angle and arrived at equation 40 (4).

$$a_{\alpha}^H = B_0 + B\langle\cos^2\theta\rangle\rho_C^{\pi}$$



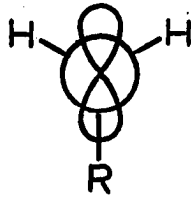
This last relationship has been applied with great success to cyclic semidiones (15) and forms the basis of the first interpretation of the data in this thesis.

$B_0$  is measured experimentally from hfsc of hydrogen atoms in the nodal plane of a  $\pi$  radical system. Such systems are shown in diagrams 41-46.

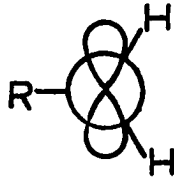
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Radical anions 41-46 clearly contain  $\alpha$  hydrogens in the nodal plane of the  $\pi$  systems. This geometry is fixed by the [2.2.2] ring system. Formation of a six carbon conjugated skeleton forces  $H_A$  in radical anion 46 to assume a position close to the nodal plane of the semidione system. The hfsc of  $H_A$  in radicals 41-43 is less than 0.1 gauss and leads to the conclusion that spin polarization is unimportant in these systems (21). The hfsc of  $H_A$  in the dicyanoethylene radical anions are not zero and have values of 0.15 and 0.225 gauss for 44 and 45, respectively (74). A spin polarization mechanism must be invoked to explain these results. It appears, therefore, that there is an anomaly in the  $H_A$  splitting constants of these radical anions. Therefore, we will use radical 46 as a standard reference compound for the determination of  $B_0$ . The hfsc for  $H_A$  in 46 is 0.21 gauss and represents the contribution of both spin polarization and possible limited rotation about the  $C_A-C_{C-O}$  bond.

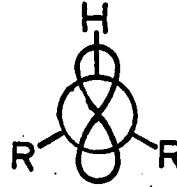
Stone and Maki also introduced the concept of rotational amplitude,  $\varphi$ , in alkyl  $\pi$  radicals.  $\varphi$  represents the residual torsional motion remaining in a system at equilibrium (4). Four possible equilibrium conformations,  $\theta_0$ , for the ethyl and isopropyl  $\pi$  radicals are shown in diagram 47.



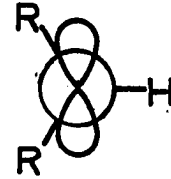
$$\theta_0 = 60^\circ$$



$$\theta_0 = 30^\circ$$



$$\theta_0 = 0^\circ$$



$$\theta_0 = 90^\circ$$

47

The angles shown are equilibrium angles,  $\theta_0$ . The time averaged  $\theta(t)$  is defined as

$$\theta(t) = \theta_0 + \varphi \sin(2\pi t/\tau)$$

48

where  $\varphi$  is the amplitude and  $\tau$  is the period of oscillation.

A term  $Q(\theta)$  is introduced where

$$Q(\theta) = B_0 + B \cos^2 \theta(t), \text{ and therefore}$$

$$Q(\theta) = B_0 + B \cos^2 [\theta_0 + \varphi \sin 2\pi t/\tau].$$

49

$\tau$  can be compared with  $\tau_0 \approx 3 \times 10^{-8}$  sec, a typical period of  $\alpha$  hydrogen hyperfine interaction. If  $\tau < \tau_0$ , then the spectrum will be resolved and  $Q(\theta)$  can be calculated by time averaging equation 49,

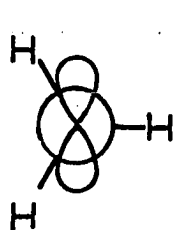
$$Q(\theta) = B_0 + B \left[ \frac{1}{\pi} \int_{-\pi/2}^{+\pi/2} \cos^2(\theta_0 + \varphi \sin x) dx \right],$$

$$Q(\theta) = B_0 + B \left[ \cos^2 \theta_0 + \cos 2\theta_0 \left( -\frac{\varphi^2}{2} + \sin \varphi \right) \right].$$

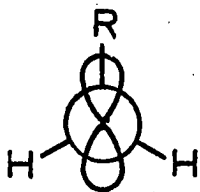
The last equation allows us to calculate  $\varphi$  for known values of  $\theta_0$ . The term  $\sin\varphi$  is small and is generally disregarded. Another measure of conformational preference is the ratio  $\underline{R}$  of the  $\alpha$  hydrogen atom splitting constant to methyl hydrogen splitting constant (4). Referring to diagram 47, a  $\theta_0 = 60^\circ$  corresponds to an  $\underline{R}$  of 0.50, and  $\theta_0 = 90^\circ$  corresponds to an  $\underline{R}$  of 0. A non-zero value of  $\underline{R}$  for an equilibrium angle of  $90^\circ$  is reflected in  $\varphi$ , the librational motion.

The alkyl radical anions studied in this work can be divided into four main classes and are represented in diagram 50. Class I is the special case of a paramagnetic center with an adjacent methyl group; class II, an adjacent methylene group; class III, an adjacent methine group; and class IV, an adjacent tertiary carbon. Class III contains three subdivisions, IIIa, IIIb, and IIIc. It includes the majority of radical anions covered. In estimating  $\theta$  in equation 40 the following assumptions were made:

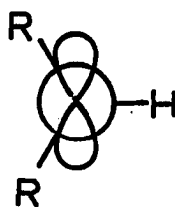
1. The product  $B_0\rho_C^\pi$  for all the above classes, I, II, III, and IV, is equal to 0.21 gauss.
2. The product  $B\rho_C^\pi$  is a constant for all cases. (This is not strictly true as conjugative and steric effects can vary  $\rho_C^\pi$ . However, corrections for these effects have been incorporated in the calculations by using the methyl hydrogen hfsc of the appropriate alkyl semidiones).



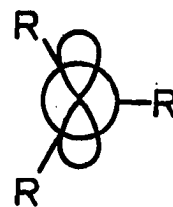
I



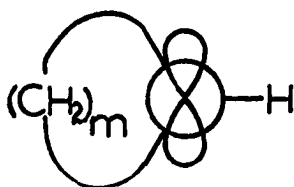
II



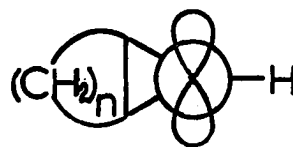
IIIa



IV



IIIb



IIIc

3. There is no steric hindrance to rotation (rotation is rapid with respect to  $\tau_0$ ) in methyl semidiones. Therefore, the average dihedral angle  $\theta$  between the axis of the carbonyl carbon  $\pi$  system and the carbon-hydrogen bond is  $45^\circ$ .

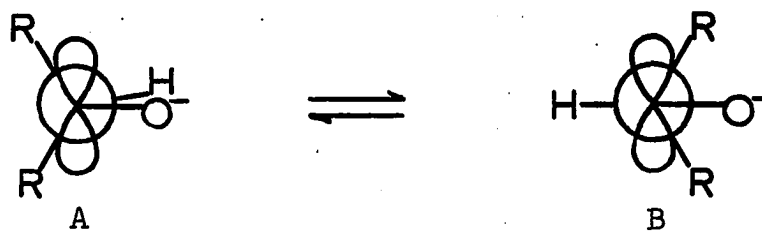
4. The conformation calculated is highly populated and assumed to be the equilibrium position demanded by  $a^H$ . In reality there is a time averaging of  $\theta$ . This  $\langle\theta\rangle$  differs from  $\theta$  and is defined as  $\theta(t)$  in eq. 48. Thus,  $\theta$  is to be used only as a qualitative measure of conformation preference.

Therefore, eq. 40 becomes:

$$\cos^2\theta = \frac{a^H - 0.21 \text{ G.}}{B\rho\pi_C}$$

For cyclopropyl methyl semidione, with a methyl group splitting of 5.88 gauss,  $B\rho\pi_C = 11.28$  gauss. Using this value,  $\theta$  for the methine hydrogen atom equals  $79.8^\circ$ . A value of 6.00 gauss for the methyl splitting was used in the calculations for the bicyclic semidiones, and the splitting constants for dimethyl semidione were used in the calculations of the radical anions in Table 6.

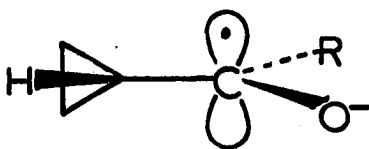
The results of these calculations, presented in Tables 4, 5 and 6, indicate marked degree of conformational preference in class III semidiones. These radicals contain an  $\alpha$  methine hydrogen atom lying in the nodal plane of the system. This gives rise to a two fold barrier of rotation as indicated by 51a--51b. A rough estimate of 1.4 kcal/mole for the height,  $V_0$ , of this barrier to internal rotation can be made (diagram 53). This estimate is based on a hfsc of 2 gauss and increases to 6 kcal/mole for an hfsc of 0.5 gauss. Thus we see that dicyclopropyl semidione exists in a highly preferred conformation with  $\theta$  of  $79.5^\circ$  and  $V_0$  equal to 6 kcal/mole. The equilibrium angle  $\theta_0$  of  $90^\circ$  and torsional rotation angle  $\phi$  of  $14.4^\circ$  reflect the bisected conformer 52.



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Table 4. Semidiones:  $R'-\overset{\ominus}{\text{C}}=\overset{\ominus}{\text{C}}-R'$

$R'$	$a_{\alpha}^{\text{H}}(\text{Gs})$	$\theta$	$\theta_{\text{O}}, \varphi$	$\underline{R}$
Cyclobutyl	2.22	64.3°	90°, 35.1°	0.396
Cyclopentyl	1.92	66.9°	90°, 31.7°	0.333
Cyclohexyl	1.88	67.2°	90°, 31.5°	0.328
Cycloheptyl	1.97	66.4°	90°, 32.4°	0.346
Cyclo-4-heptenyl	2.08	65.6°	90°, 33.4°	0.365
Cyclopropyl	0.57	79.5°	90°, 14.4°	0.097
2,2-Dimethylcyclopropyl	1.49	70.2°	90°, 27.4°	0.257
6-Bicyclo[3.1.0]hexyl	0.75	77.5°	90°, 18.6°	0.125
7-Bicyclo[4.1.0]heptyl	0.52	80.6°	90°, 13.2°	0.087
8-Bicyclo[5.1.0]octyl	0.49	80.9°	90°, 12.6°	0.082



52

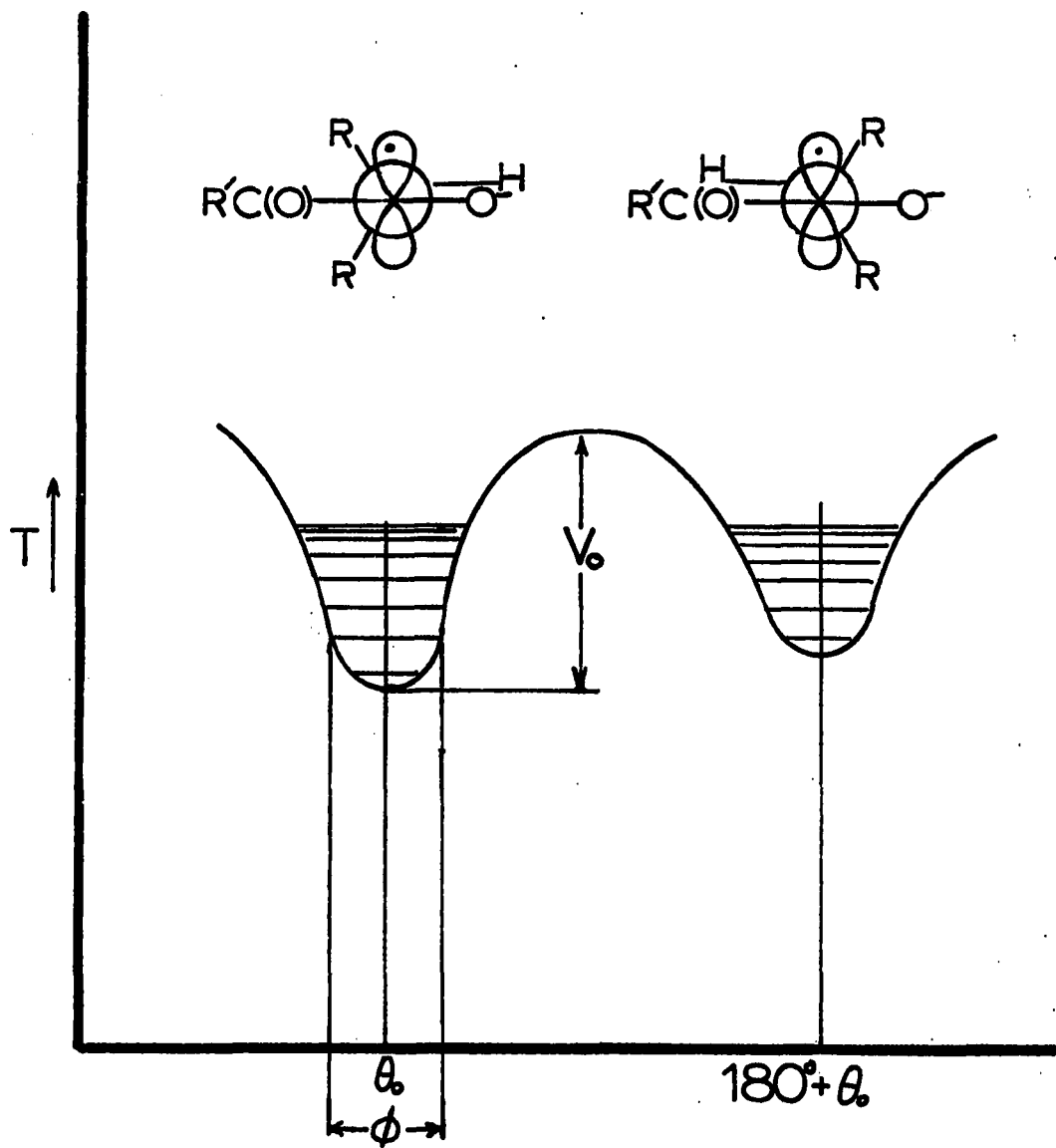




Table 5. Semidiones:  $R'-C(=O)-C(=O)CH_3$

$R'$	$a_{\text{methyl}}^H$ (Gs)	$a_{\alpha}^H$ (Gs)	$\theta$	$\theta_o, \varphi$	$\underline{R}$
Cyclobutyl	5.55	2.11	65.1°	90°, 34.1°	0.380
Cyclopentyl	5.77	1.92	66.9°	90°, 31.7°	0.333
Cyclohexyl	5.73	1.73	68.3°	90°, 30.1°	0.302
Cyclooctyl	5.85	1.94	66.9°	90°, 31.7°	0.332
Cyclopropyl	5.88	0.57	79.5°	90°, 14.4°	0.097
2,2-Dimethylcyclopropyl	5.79	1.49	70.2°	90°, 27.4°	0.257
7-Bicyclo[4.1.0]heptyl	6.00	0.52	80.6°	90°, 13.2°	0.087

On the basis of UV and NMR studies of cyclopropylcarbinyl systems, the three-membered ring is expected to stabilize adjacent half-filled or empty orbitals (37-40). Thus, structure 54b is expected to be more important than structure 54a. De-localization is predicted by the Walsh picture of cyclopropane.

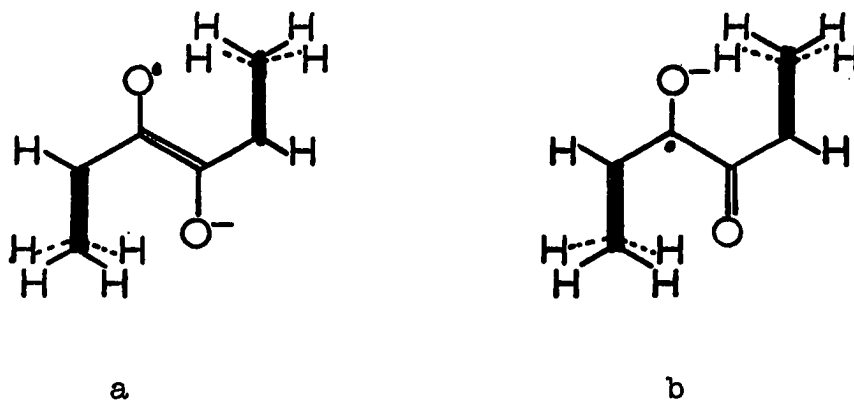


Table 6. Semidiones:  $R'-\overset{\overset{O^-}{|}}{C}=\overset{\underset{O}{|}}{C}-R'$

$R'$		$a_{\alpha}^H$ (Gs)	$a_{\beta}^H$ (Gs)	$\theta$	$\theta_o, \varphi$	$\underline{R}$	Ref.
CH <sub>3</sub>	trans	5.70		45°	45°	1.00	16
	cis	6.90		45°	45°	1.00	16
CH <sub>2</sub> CH <sub>2</sub>	trans	4.90		49.2°	60°, 36.7°	0.86	16
	cis	6.00		48.3°	60°, 36.4°	0.87	16
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub>	trans	4.60	0.25	50.8°	60°, 33.7°	0.81	16
	cis	5.60		50.6°	60°, 33.6°	0.81	16
(CH <sub>3</sub> ) <sub>2</sub> - CHCH <sub>2</sub>	trans	4.30	0.26	52.4°	60°, 30.6°	0.76	16
	cis	5.30		52.0°	60°, 30.7°	0.77	16
(CH <sub>3</sub> ) <sub>3</sub> - CCH <sub>2</sub>	trans	3.50		56.8°	60°, 19.4°	0.61	
	cis	4.50		55.4°	60°, 23.2°	0.65	
(CH <sub>3</sub> ) <sub>2</sub> CH		2.02	0.03	66.0°	90°, 32.9°	0.35	
(CH <sub>3</sub> CH <sub>2</sub> )CH		1.09	0.13	73.6°	90°, 22.9°	0.19	
(CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> )CH		0.95		75.0°	90°, 21.0°	0.17	
(CH <sub>3</sub> ) <sub>3</sub> C			0.29				16

A partial valence bond picture of this delocalization is given in diagram 25 and is repeated below.

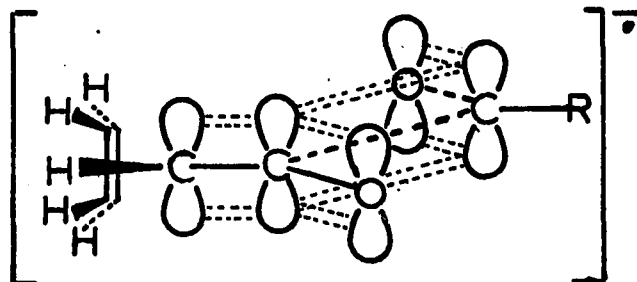
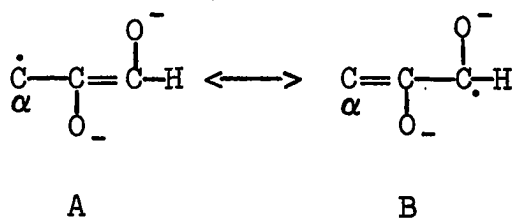


Diagram 25 depicts a 5 atom, 7 electron  $\pi$  system. McLachlan spin density calculations were performed on the structure 25 using the following carbonyl parameters:  $\alpha_0 = \alpha_C + B_{CC}$ ,  $B_{CO} = B_{CC}$ . That  $\alpha$  carbon was treated as a heteroatom with  $\alpha_C = \alpha_C + B_{CC}$  and  $\alpha = \alpha_C + 0.9 B_{CC}$  (75). The results predicted the resonance forms in diagram 55.



55

Structure 54b places electron spin density on carbon as opposed to oxygen, 54a. This is expected to result in increased methyl hydrogen splitting in the cyclopropyl methyl semidiones. Table 4 containing the methyl splittings for a series of mixed semidiones supports this hypothesis. The  $a_{\text{methyl}}^{\text{H}}$  for R'=cyclohexyl, 2,2-dimethylcyclopropyl, cyclopropyl, and 7-bicyclo[4.1.0]heptyl increases from 5.73 to 5.79 to 5.88 to 6.00 gauss, respectively. This trend is predicted by the above spin density calculations which places a high spin density on the carbonyl carbon adjacent to the methyl group in cyclopropyl semidione. The change from 5.73 to 6.00 gauss represents an increase of 1.1% in the electron spin density on the carbonyl carbon. This estimate led to an investigation of  $C^{13}$  splittings, preliminary results of which are presented in the next section. However, we have

been unable to devise a practical scheme for the synthesis of labelled cyclopropyl semidiones.

Bauld, Gordon, and Zoeller have reported two cyclopropyl radical anions with "symmetrical" cyclopropyl conformations, 56.

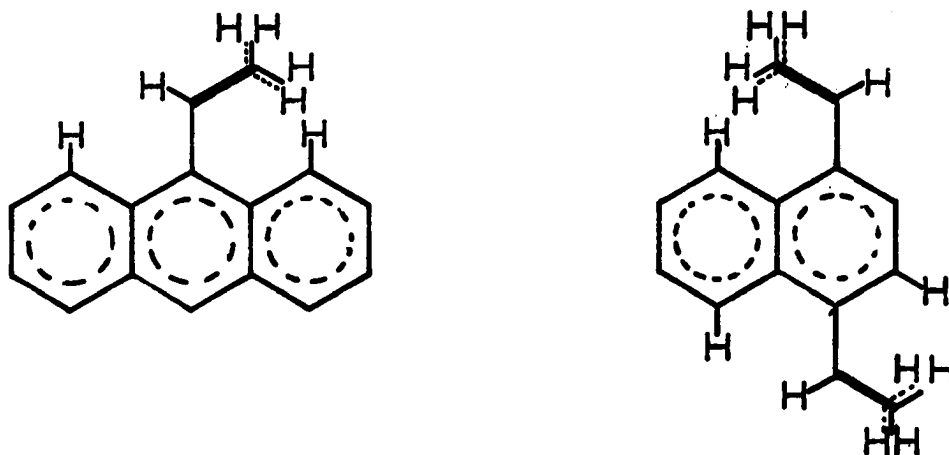


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The evidence for this assertion was an  $\underline{R}$  greater than 1.00 (10). The first radical was that of 9-cyclopropylanthracene with an  $a_{\alpha}^H$  of 6.64 gauss as compared with 0.62 gauss for 9-isopropylanthracene. An investigation of Molecular Framework Models (Prentice-Hall, Inc., Englewood Cliffs, N. J.) of this system revealed extensive steric hindrance in the bisected cyclopropyl conformation. The methyl groups on the isopropyl group, unlike the methylenes on the three membered ring, can extend outward from the faces of the anthracene system. The second radical reported is 1,4-dicyclopropyl-naphthalene radical anion. There is again more steric hindrance in the bisected than the symmetrical conformations (diagram 57). However, it is also possible that the radical anion of 1,4-dicyclopropylnaphthalene is unstable under

reducing conditions. We have shown that cycloprop[a]acenaphthylene and 1-methylacenaphthylene both yield the same radical when reduced either by electrolysis or with potassium in tetrahydrofuran.

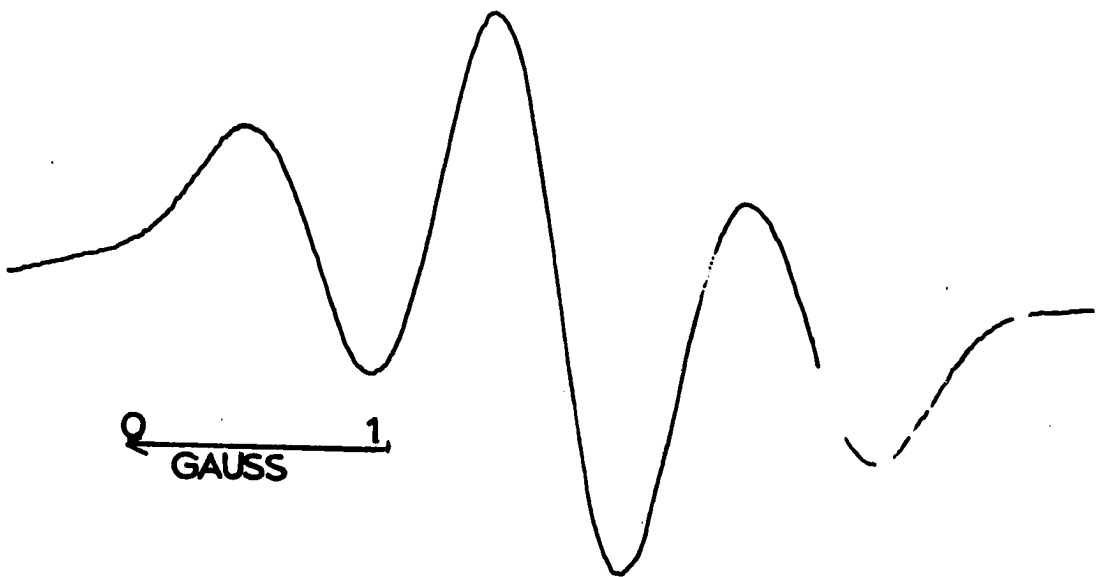
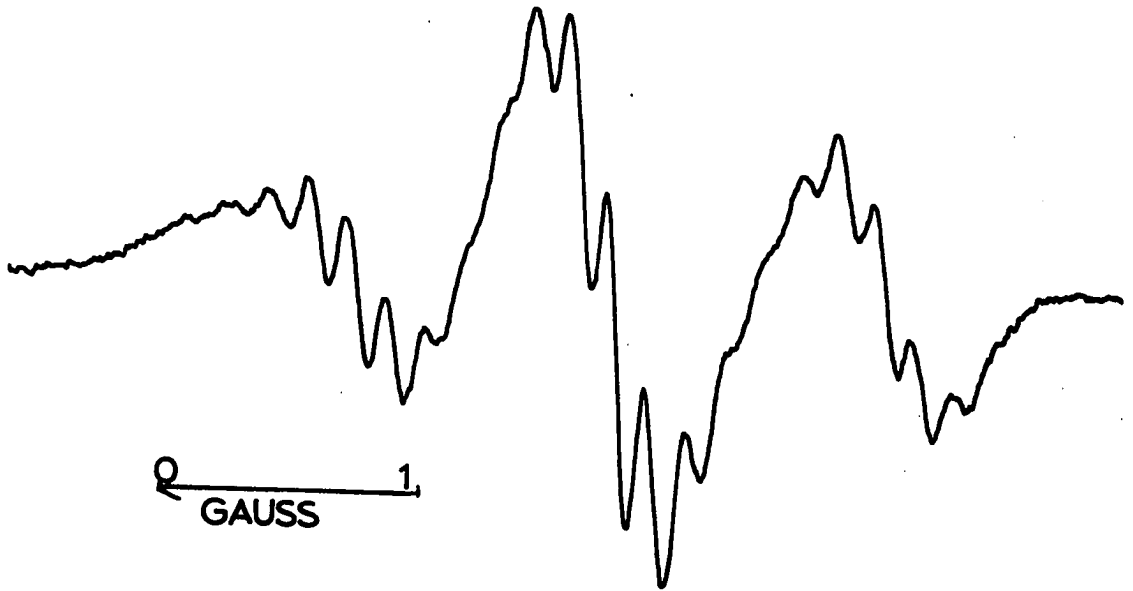
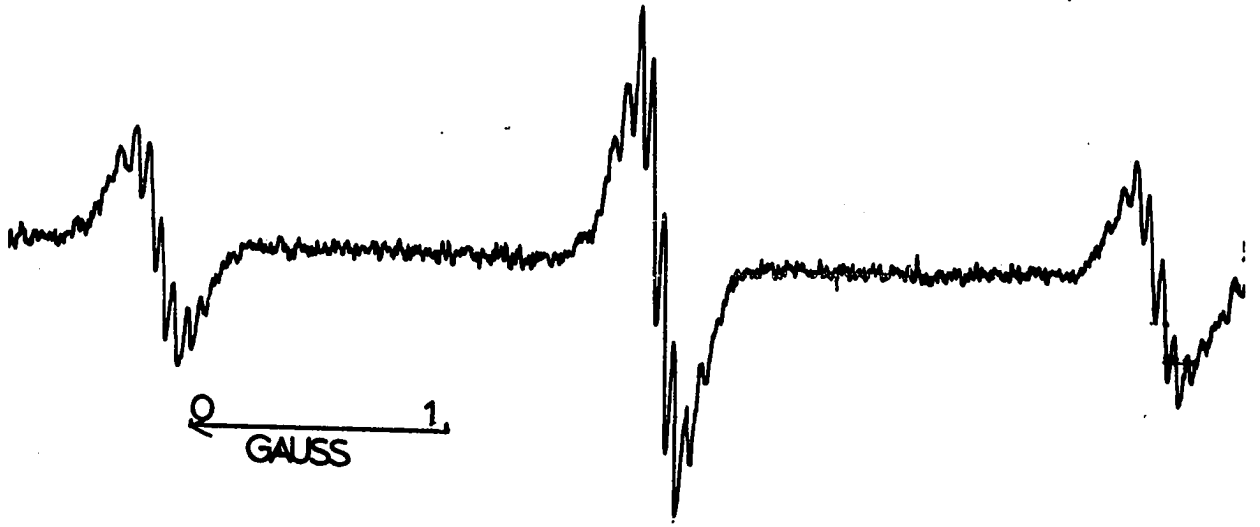
The effect of bulky substituents on the  $\alpha$  methine hydrogen atom splitting was investigated by synthesizing the series



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diisopropyl, di-3-pentyl, and di-4-heptyl semidiones (Figure 22). It was thought that di-3-pentyl semidione would be a good model system for dicyclopropyl semidione. Steric hindrance to rotation caused by the methylene groups of the three membered ring is approximated by the freely rotating ethyl groups of di-3-pentyl semidione. Indeed, the increase in length of the branched chain does affect the  $\alpha$  methine proton splitting constant. However, the decrease from 2.02 to 0.95 gauss does not approach the 0.57 gauss splitting of the cyclopropyl ring methine hydrogen. The decrease in splitting constant in this series is caused mainly by steric

- Figure 22. (a) First-derivative ESR spectrum of diisopropyl semidione (top) in DMSO.
- (b) First-derivative ESR spectrum of di-3-pentyl semidione (middle) in DMSO.
- (c) First-derivative ESR spectrum of di-4-heptyl semidione (bottom) in DMSO.

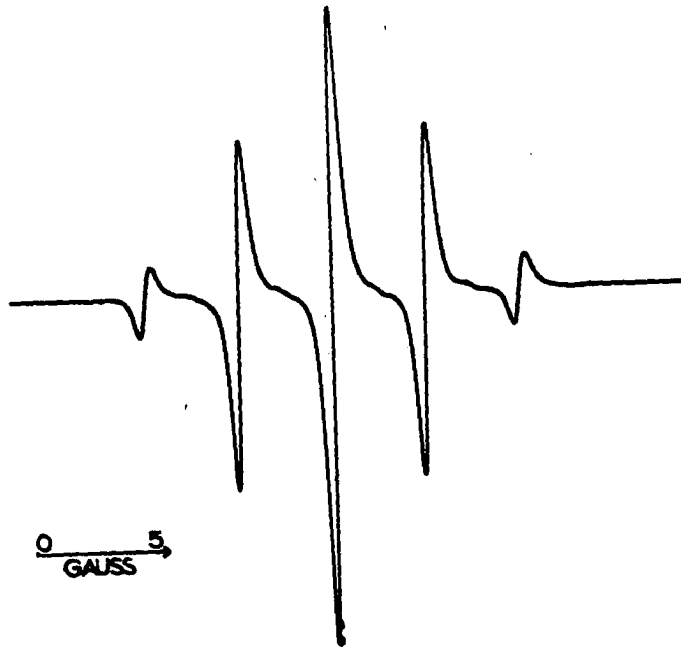
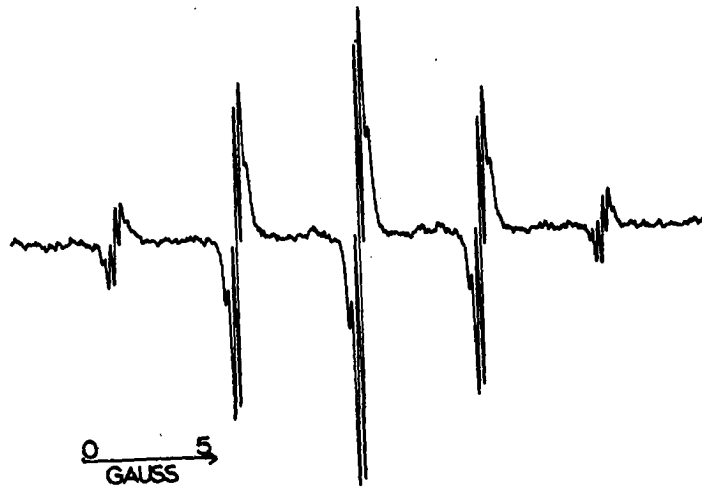


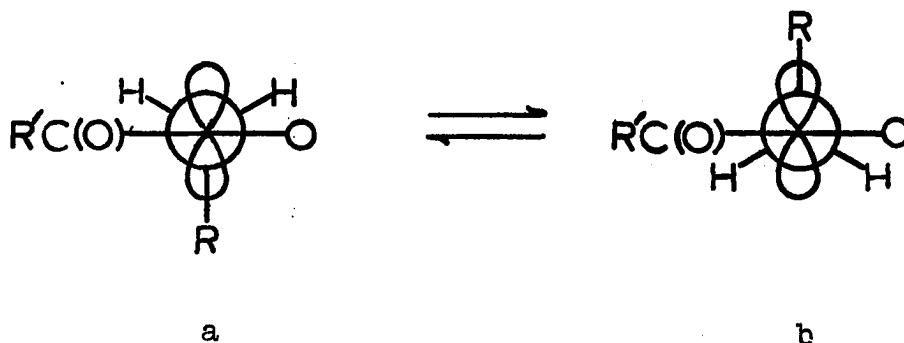
hindrance from free rotation of the branched chain. This is evident from investigating the  $\alpha$  methine splitting of the semidione series of Table 6, R' equal to cyclobutyl, cyclopentyl, cyclohexyl and cycloheptyl. In this series the  $\alpha$  methine hydrogen hfsc remains relatively constant in spite of increasing ring size.

The last set of semidiones studied in this work is the class II radicals (diagram 50) containing an  $\alpha$  methylene group. The straight chain series of diethyl, dipropyl, ... didecyl semidiones has been investigated (16). The  $\alpha$  methylene hydrogen atom splitting decreases from 4.9 in diethyl to a relatively constant 4.6-4.7 gauss in dipropyl, dibutyl, .... didecyl. This seems to indicate that steric hindrance in this system is determined by rotation about the  $C_{\beta}-C_{\gamma}$  bond. Increasing the number of  $\gamma$  methyl groups in Table 6 semidiones, where R' equals  $CH_3CH_2-$ ,  $CH_3CH_2CH_2-$ ,  $(CH_3)_2CH_2CH_2-$ , and  $(CH_3)_3CCH_2-$ , has a marked effect on the methylene splitting (Figure 23). The respective splitting constants 4.90, 4.60, 4.30, and 3.50 gauss reflect a conformational preference. The conformers with the least steric interaction are 58a and 58b. They represent a two-fold internal barrier to rotation (diagram 53). The torsional amplitude decreases from  $37^\circ$  for R' equal to  $CH_3CH_2-$  to  $19^\circ$  for R' equal to  $(CH_3)_3CCH_2-$ . In the quantum mechanical approximation of Stone and Maki, the barrier to rotation,  $V_0$ ,



- Figure 23. (a) First-derivative ESR spectrum of dipropyl semidione (top) in DMSO.
- (b) First-derivative ESR spectrum of diisobutyl semidione (middle) in DMSO.
- (c) First-derivative ESR spectrum of dineopentyl semidione (bottom) in DMSO.





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increases from 0.5 kcal/mole for  $R'$  equal to  $\text{CH}_3\text{CH}_2-$  to 3 kcal/mole for  $R'$  equal to  $(\text{CH}_3)_3\text{CCH}_2-$ . Large values of  $V_0$  reflect a strong dependence on temperature.

Stone and Maki predicted that the  $\alpha$  hydrogen atom splitting constant is directly proportional to  $V_0/T$ , assuming that  $V_0$  is not a function of temperature (4). Figure 24 represents a graph of  $a_{\alpha}^{\text{H}}$  versus temperature for semidiones in Table 6, where  $R' = (\text{CH}_3)_2\text{CH}-$ ,  $(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{CH}-$ ,  $(\text{CH}_3)_2\text{CHCH}_2-$  and  $(\text{CH}_3)_3\text{C}-\text{CH}_2-$ . The radicals were generated in *N,N*-dimethylformamide (DMF) and studied with a Varian V-4500 spectrophotometer equipped with a Varian Associates V-4540 variable temperature controller. The slopes of the lines obtained are equal to  $KV_0$  and agree qualitatively with the estimates of  $V_0$ . The estimates of  $V_0$  and the calculated slopes are presented in Table 7. Semidione,  $R' = \text{CH}_3\text{CH}_2-$ , was studied with the variable temperature controller by Mr. D. Lawson. He found little

Figure 24. Graph of  $\alpha$  hydrogen atom splitting constants as a function of temperature for the following semidiones in DMF:

$\Delta$  = Diisobutyl semidione

$\times$  = Di-neopentyl semidione

$\square$  = Diisopropyl semidione

$\circ$  = Di-4-heptyl semidione

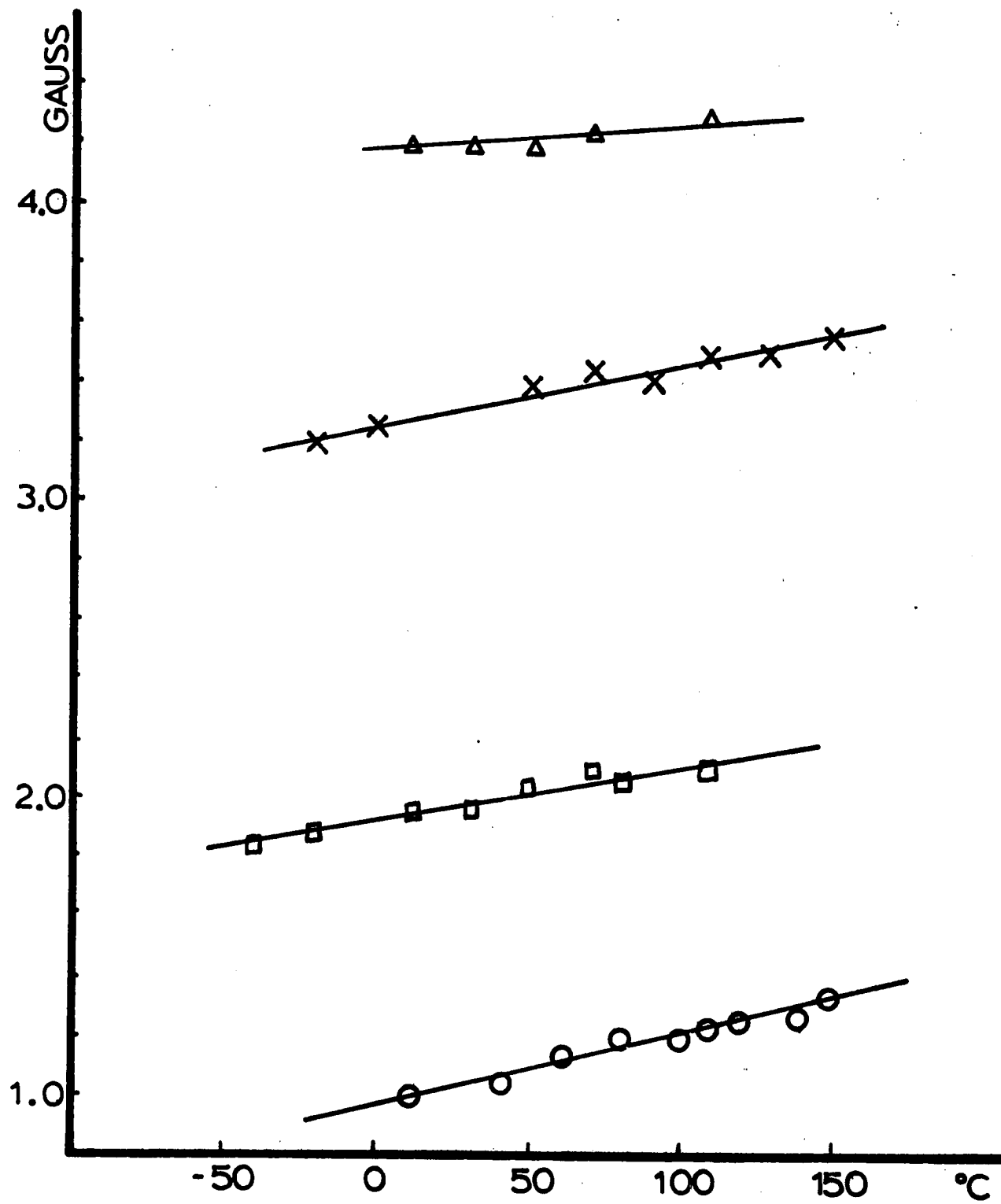
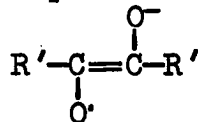


Table 7. Temperature dependence and estimation of  $V_0$  in semidiones:

R'	$a_\alpha^a$ (gauss)	$KV_0^b$ (gauss/deg)	$V_0^c$ (kcal/mole)
CH <sub>3</sub> CH <sub>2</sub>	4.90	0	0.5
(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub>	4.30	1.0 x 10 <sup>-3</sup>	0.9
(CH <sub>3</sub> ) <sub>3</sub> CCH <sub>2</sub>	3.50	2.2 x 10 <sup>-2</sup>	3.0
(CH <sub>3</sub> ) <sub>2</sub> CH	2.02	1.9 x 10 <sup>-2</sup>	1.4
(CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> CH	0.95	2.4 x 10 <sup>-2</sup>	3.0

<sup>a</sup>Splitting constants of trans isomer measured in DMSO solution at 25°.

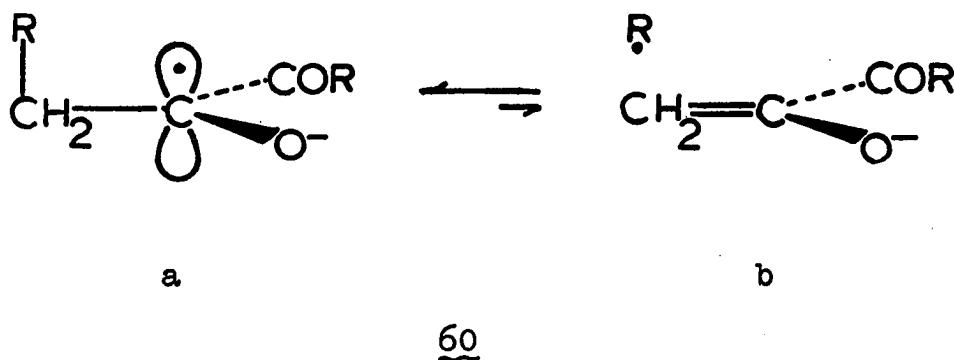
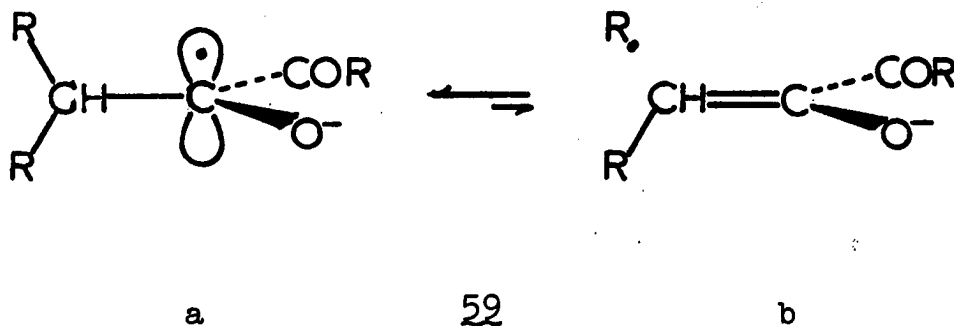
<sup>b</sup>Slope of  $\alpha$  splitting constant versus temperature.

<sup>c</sup>Estimated from Figure 3 in reference (4).

temperature dependence in the ESR spectra of the semidione. This is indicated in Table 7 by a zero slope. Semidiones, R' = (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>CH-, failed to give a stable radical in DMF below 40° or above 85° and could not be studied. Experimental limitations also prevented the study of dicyclopropyl semidione. The special cell (Varian Associates V-4548-1-aqueous sample cell) used in the variable temperature controller reduces linewidth resolution to about 0.2 gauss, and in the case of dicyclopropyl semidione produces only a broad line. Consequently, no temperature dependence could be

detected in this spectrum.

The conformation effects found in the semidiones of Table 6 may be explained in terms of hyperconjugative structures, such as 59b and 60b.



This mechanism predicts that the stability of  $R^\cdot$  will determine the stability of the radical anion and the degree of conformational preference. The stability of  $R = \text{CH}_3^\cdot < R = \text{CH}_3\text{CH}_2^\cdot < R = \text{CH}_3\text{CH}_2\text{CH}_2^\cdot$  in diagram 59 and of  $R = \text{CH}_3^\cdot < R = \text{CH}_3\text{CH}_2^\cdot < R = (\text{CH}_3)_2\text{CH}^\cdot < R = (\text{CH}_3)_3\text{C}^\cdot$  in diagram 60 explains the trend in the  $a_{\alpha}^{\text{H}}$  in Table 6. Qualitatively, the acyloins  $(\text{CH}_3)_3\text{C}-\text{CH}_2-\text{CO}-\text{CH}(\text{OH})-\text{CH}_2-\text{C}(\text{CH}_3)_3$  and  $(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{CH}-\text{CO}-\text{CH}(\text{OH})-$

$\text{CH}(\text{CH}_3\text{CH}_2\text{CH}_2)_2$  gave very concentrated solutions of radical anions. These two semidiones appeared to be more stable than the other diacyclic radicals studied.

### Carbon-13 Splitting Constants

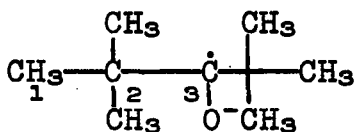
Thus far in our calculations we have assumed that the carbonyl carbon  $\pi$  spin density ( $\rho_\pi$ ) is constant for all trans dialkyl semidiones. Corrections for varying spin density have been made whenever the appropriate methyl substituted semidione was available. However, this approximation involves the assumption that the carbonyl carbons in mixed semidiones are equivalent. This is not expected to be valid. In a bicyclo[4.1.0]heptyl methyl semidione the methyl splitting indicated about 1% more spin density on the methyl carbonyl carbon than in dimethyl semidione. McLachlan spin density calculations predicted this increase on the basis of cyclopropyl ring delocalization.

Spin density has been estimated in semidione systems by McLachlan and Hückel molecular orbital calculations (76). These calculations rely on accurate bond angles and bond distances which for the semidione system are unavailable (77). Consequently this method is good only for a qualitative picture of spin distribution. Experimentally,  $\rho_\pi$  can be approximated by measuring the appropriate  $^{13}\text{C}$  splitting constants.

The first reported measurements of  $^{13}\text{C}$  hyperfine splittings were made by Hirota and Weissman (78) and by Reitz, Dravnieks, and Wertz (79). Hirota and Weissman

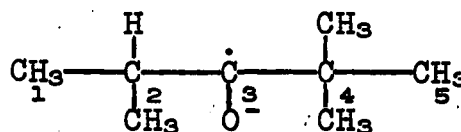


reported the spectra from the potassium ketyls of di-t-butyl ketone and t-butyl isopropyl ketone. Their results are shown in 61 and 62.



$$a_1^C = 7.6 \text{ gauss}$$

$$a_3^C = 49.6 \text{ gauss}$$

61

$$a_1^C = 13 \text{ gauss}$$

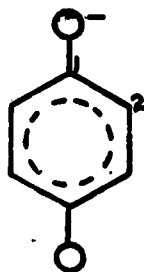
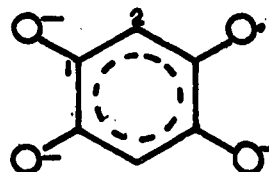
$$a_3^C = 49.8 \text{ gauss}$$

62

Reitz et al., reported the  $^{13}\text{C}$  hfsc for the p-benzosemiquinone (diagram 63) and 2,5-dioxy-1,4-benzosemiquinone (diagram 64). These results are shown in 63 and 64.

$$a_1^C = \geq 0.1 \text{ gauss}$$

$$a_2^C = \geq 0.6 \text{ gauss}$$

63

$$a_1^C = 2.82 \text{ gauss}$$

$$a_2^C = 6.62 \text{ gauss}$$

64

The carbonyl  $\rho^\pi$ , however, is solvent dependent (4, 80, 81). Therefore, the original calculations were often misleading (82-84).

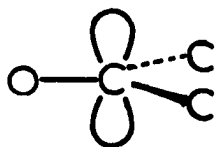
Karplus and Fraenkel developed a general theory relating  $^{13}\text{C}$  hyperfine splittings to  $\rho^\pi$ . According to this theory, the magnitude of the  $^{13}\text{C}$  splitting depends upon the pi spin

density at the carbon in question as well as at the neighboring carbons (85, 86). This relationship is expressed as

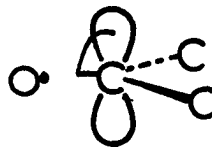
$$a^C = (S^C + \sum_{i=1}^3 Q_{CX_i}^C) \rho^\pi + \sum_{i=1}^3 Q_{X_i}^C$$

65

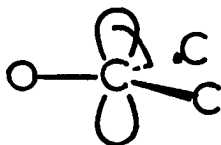
where  $S^C$  is the contribution from polarization of the 1s electrons.  $Q_{CX_i}^C$  is a factor representing the contribution of the 2s electrons to the splitting constant of C by  $\rho^\pi$  on atom C which is bonded to  $X_i$ .  $Q_{X_i}^C$  represents the contribution to the splitting constant of C from spin density on  $X_i$ . This can be demonstrated by valence-bond structure for a  $\text{COC}_2$  fragment (diagram 66).



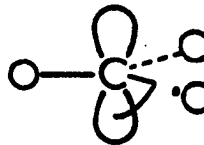
a



b



c



d

66

Structure 66a represents the ground state configuration of a  $\pi$  radical. Structures 66b-66d represent the excited states with one broken sigma bond. In this simple picture  $Q_{CO}^C$  corresponds to structure 66b and is the contribution from polarization of the 2s electrons on C.

Das and Fraenkel (87) applied the Karplus-Fraenkel equation to the semiquinones studied by Rietz, et al., and determined  $Q_{OC}^C = -27.1$  and  $Q_{C'C}^C = -20.9$ . Studies of ethyl radicals led to the values of  $Q_{CC'}^C = 30$  and  $Q_{C'C}^C = -20.9$  (82, 88). Other studies of  $^{13}C$  splittings have been performed on hydrocarbons (88), nitroxides (89-91), and alkyl substituted semiquinones (92). Studies of semidione systems have thus far been limited to detection of  $^{13}C$  in natural abundance (93, 94). The assignments in these cases have been based on McLachlan calculations and intensity measurements. Both methods while useful often have led to erroneous results (87, 89, 93-95). Therefore, diisopropyl acyloins substituted in the 2 and 3 positions with  $^{13}C$  were synthesized. 2-Chloropropane-2- $^{13}C$  (Volk Radiochemical Company, 51.5%  $^{13}C$ ) was converted to the Grignard reagent and reacted with isobutyraldehyde cyanohydrin to yield diisopropyl acyloin-2- $^{13}C$ . Isopropylmagnesium chloride was carbonated with carbon dioxide- $^{13}C$  (prepared from 30 grams of barium carbonate- $^{13}C$ , certified by Merck, Sharp, and Dohme of Canada, Ltd., to contain one gram  $^{13}C$ ; 53%  $^{13}C$ ) to yield isobutyric

acid-1- $^{13}\text{C}$ . The acid was converted to the ethyl ester with triethyl phosphate and condensed with sodium sand in ether to yield diisopropyl acyloin-3- $^{13}\text{C}$ . The ESR spectra of unlabeled diisopropyl semidione is shown in Figure 25a. Only one set of  $^{13}\text{C}$  splittings, 4.00 gauss, is detectable. Comparison with the spectrum of diisopropyl semidione-2- $^{13}\text{C}$  (Figure 25b) shows that this splitting is due to the  $\alpha$  carbons. The spectrum of diisopropyl semidione-3- $^{13}\text{C}$  (Figure 26a) displays the triplet methine hydrogen atom splitting and a small doublet splitting of 0.8 gauss. The high field line of the doublet is considerably broadened with respect to the low field line. This broadening has been attributed to high spin density (19).

Das and Fraenkel proposed that line broadening determines the sign of the product  $a_{1\rho_1}^{\text{C}} \pi$  (87). The sign is positive when the upfield satellite is wider and vice versa. As the carbonyl carbon is expected to have a positive spin density, the  $^{13}\text{C}$  hyperfine splitting constant is positive (96-99). A small solvent effect was observed when diisopropyl semidione-3- $^{13}\text{C}$  was generated in DME. The signal, however, was too weak for accurate measurement (Figure 26b). The sign of the  $\alpha$  carbon splitting constant could not be determined from the spectrum. The methyl carbons,  $\text{C}_1$ , are expected to exhibit natural abundance  $^{13}\text{C}$  splittings. This is analogous to di-t-butyl ketyl and di-t-butyl nitroxide (89).

Figure 25. (a) First-derivative ESR spectrum of unlabeled diisopropyl semidione (top) in DMSO displaying natural abundance  $^{13}\text{C}$  splittings. (b) First-derivative ESR spectrum of diisopropyl semidione-2- $^{13}\text{C}$  (bottom) in DMSO.

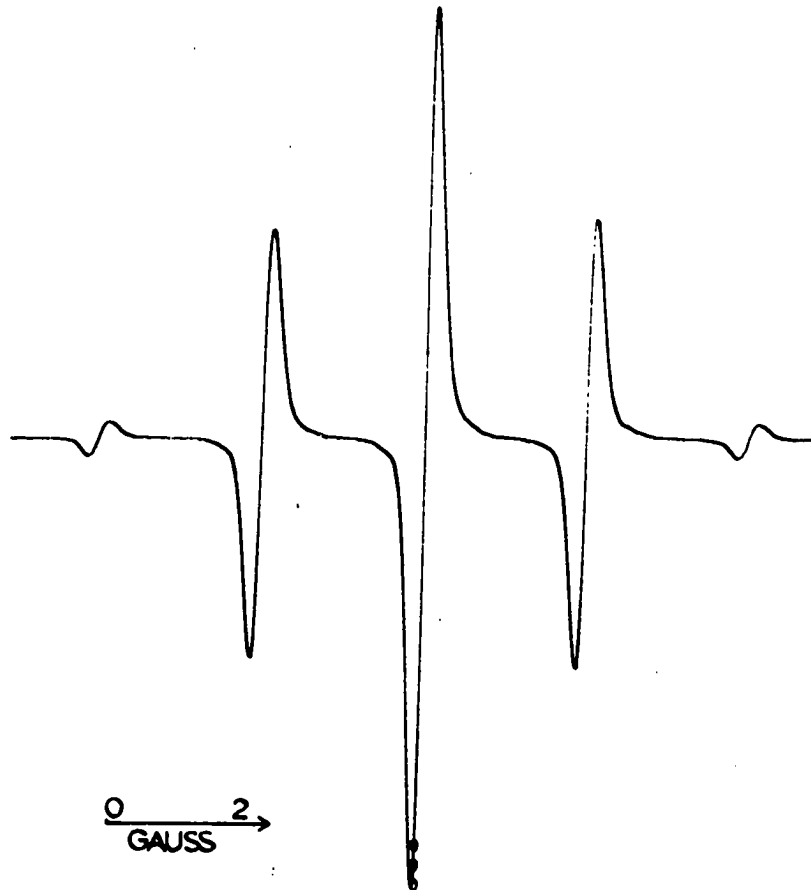
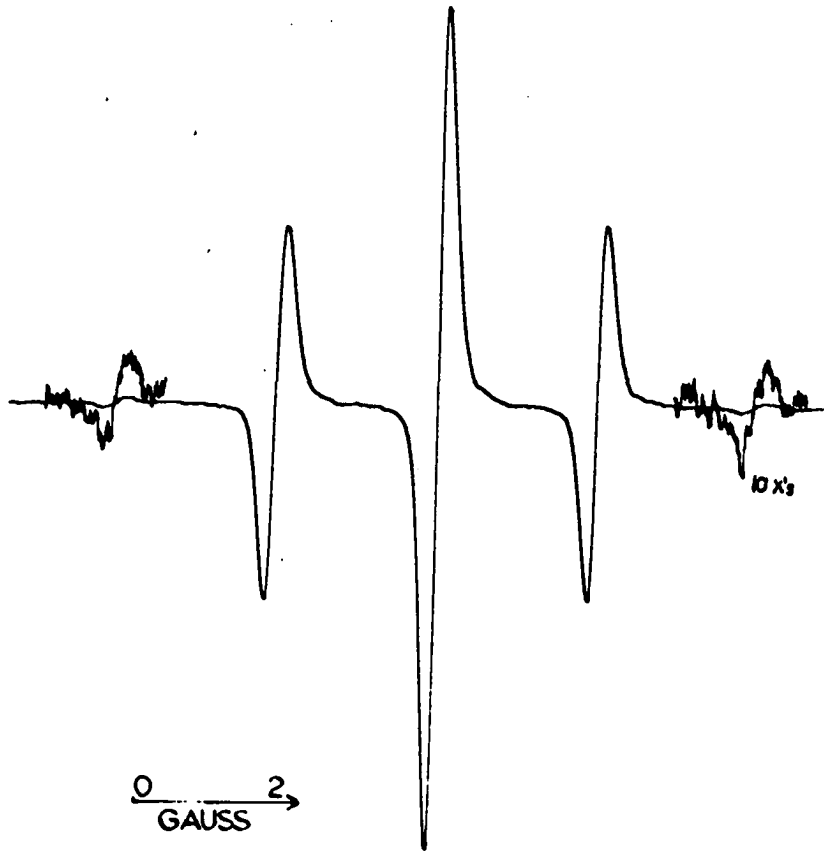
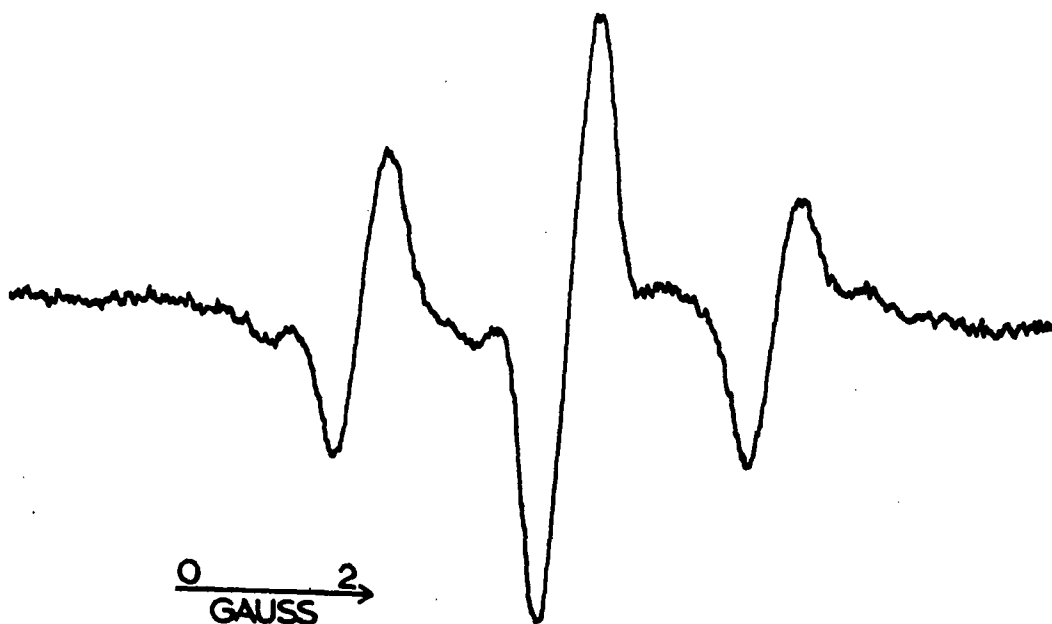
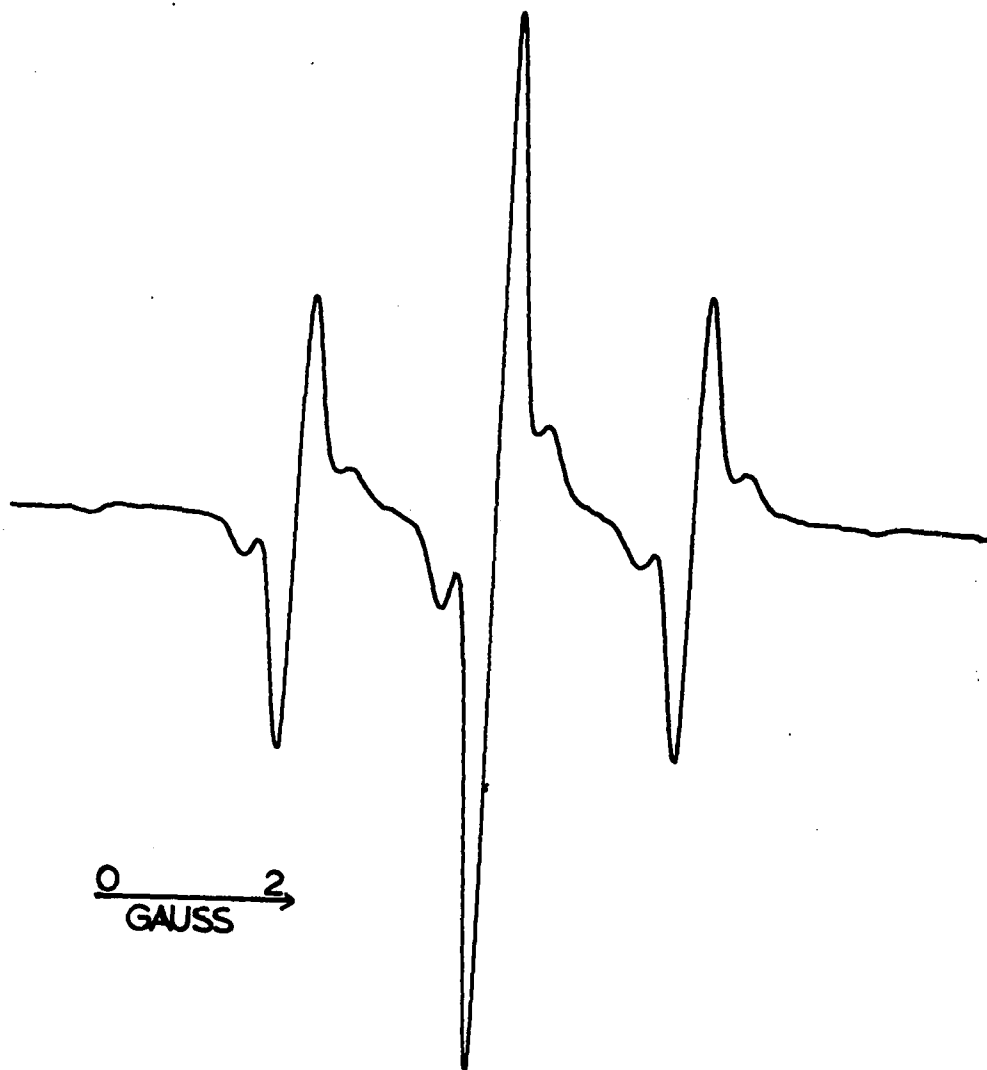


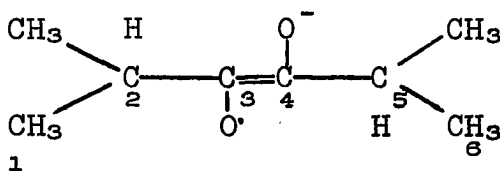
Figure 26. (a) First-derivative ESR spectrum of diisopropyl semidione- $\beta$ - $^{13}\text{C}$  (top) in DMSO.  
(b) First-derivative ESR spectrum of diisopropyl semidione- $\beta$ - $^{13}\text{C}$  (bottom) in DME.





The  $^{13}\text{C}$  hfsc of the methyl carbons of these radicals have been reported. Therefore, the  $C_1$  splitting constants in diisopropyl semidione are either hidden beneath the  $C_2$  satellites or are smaller than 0.8 gauss.

If the Karplus-Fraenkel equation is applied to the diisopropyl semidione system, 67,  $\rho^\pi$  at carbonyl carbon and on oxygen can be estimated.



67

$$a^{C_3} = (S^C + Q_{C_3C_2}^{C_3} + Q_{C_3C_4}^{C_3} + Q_{C_3O}^{C_3})\rho_{C_3}^\pi + Q_{C_2C_3}^{C_3}\rho_{C_2}^\pi + Q_{C_4C_3}^{C_3}\rho_{C_4}^\pi + Q_{OC_3}^{C_3}\rho_O^\pi$$

The two carbonyl positions are equivalent by symmetry.

Therefore,  $\rho_{C_3}^\pi = \rho_{C_4}^\pi$  and  $Q_{C_3C_4}^{C_3} = -Q_{C_3C_2}^{C_3}$ . The equation reduces to

$$a^{C_3} = (S^C + Q_{C_3C_2}^{C_3} + Q_{C_3O}^{C_3})\rho_{C_3}^\pi + Q_{C_2C_3}^{C_3}\rho_{C_2}^\pi + Q_{OC_3}^{C_3}\rho_O^\pi.$$

68

Next the assumption is made that  $\rho_{C_2}^\pi = 0$ . This is not strictly true as estimates of  $\rho_{C_2}^\pi$  can vary between 0.087 and 0.001 depending upon the method of calculation. The first estimate is based on the splitting of the methyl radical, 23 gauss, (100), and the second of the hydrogen atom, 508 gauss, (101).

These last two values are used as  $Q$  values in the McConnell relation (102),

$$a_i^H = Q_{CH}^H \rho_i^\pi$$

In this equation  $a_i^H$  is the  $\alpha$  methine proton splitting of 2.0 gauss. Therefore, the equation 68 reduces to

$$a^{C_3} = (S^C + Q_{C_3C_2}^{C_3} + Q_{C_3O}^{C_3}) \rho_{C_3}^\pi + Q_{OC_3}^{C_3} \rho_O^\pi$$

where  $S^C = -12.7$ .  $Q_{C_3C_2}^{C_3}$  represents an interaction between an  $sp^2$  and  $sp^3$  carbon and is approximated by  $Q = 30$  for the ethyl radical (100). The other  $Q$  values,  $Q_{C_3O}^{C_3} = 17.7$  and  $Q_{OC_3}^{C_3} = -27.1$ , have been estimated by Das and Fraenkel (87) for the semiquinone system. It is assumed, therefore, that the interactions between oxygen and carbon in the semiquinone and trans semidione systems are similar. With these substitutions, the equation can be reduced to two unknowns.

$$a^C = (-12.7 + 30 + 17.7) \rho_{C_3}^\pi - 27.1 (\rho_O^\pi)$$

$$a^{C_3} = 35 \rho_{C_3}^\pi - 27.1 \rho_O^\pi$$

Since the assumption  $\rho_{C_2}^\pi = 0$  has been made  $2(\rho_{C_3}^\pi + \rho_O^\pi) = 1.00$ . An  $a^{C_3}$  of 0.8 gauss yields  $\rho_{C_3}^\pi = 0.23$  and  $\rho_O^\pi = 0.27$ .

A similar calculation can be performed for  $a^{C_2}$ , however the approximation that  $\rho_{C_2}^\pi$  and  $\rho_C^\pi$  are negligible becomes severe.

$$a^{C_2} = (S^C + 2Q_{C_1C_2}^{C_2} + Q_{C_2H}^{C_2} + Q_{C_2C_3}^{C_2}) \rho_{C_2}^\pi + Q_{C_3C_2}^{C_2} \rho_{C_3}^\pi + 2Q_{C_2C_1}^{C_2} \rho_{C_1}^\pi$$

Equation 69 reduces to 70.

$$a^{C_2} = Q_{C_3C_2}^{C_2} \rho_{C_3}^{\pi}$$

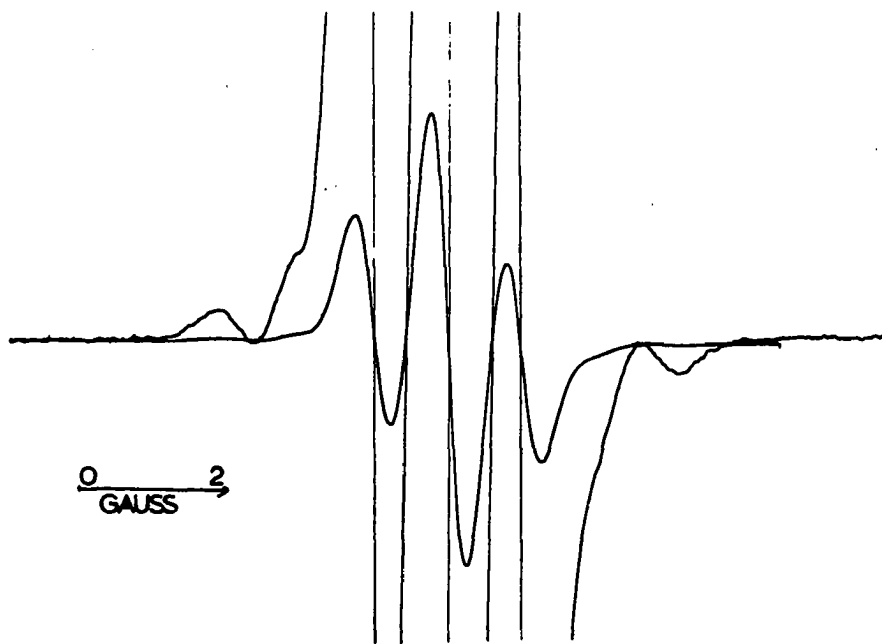
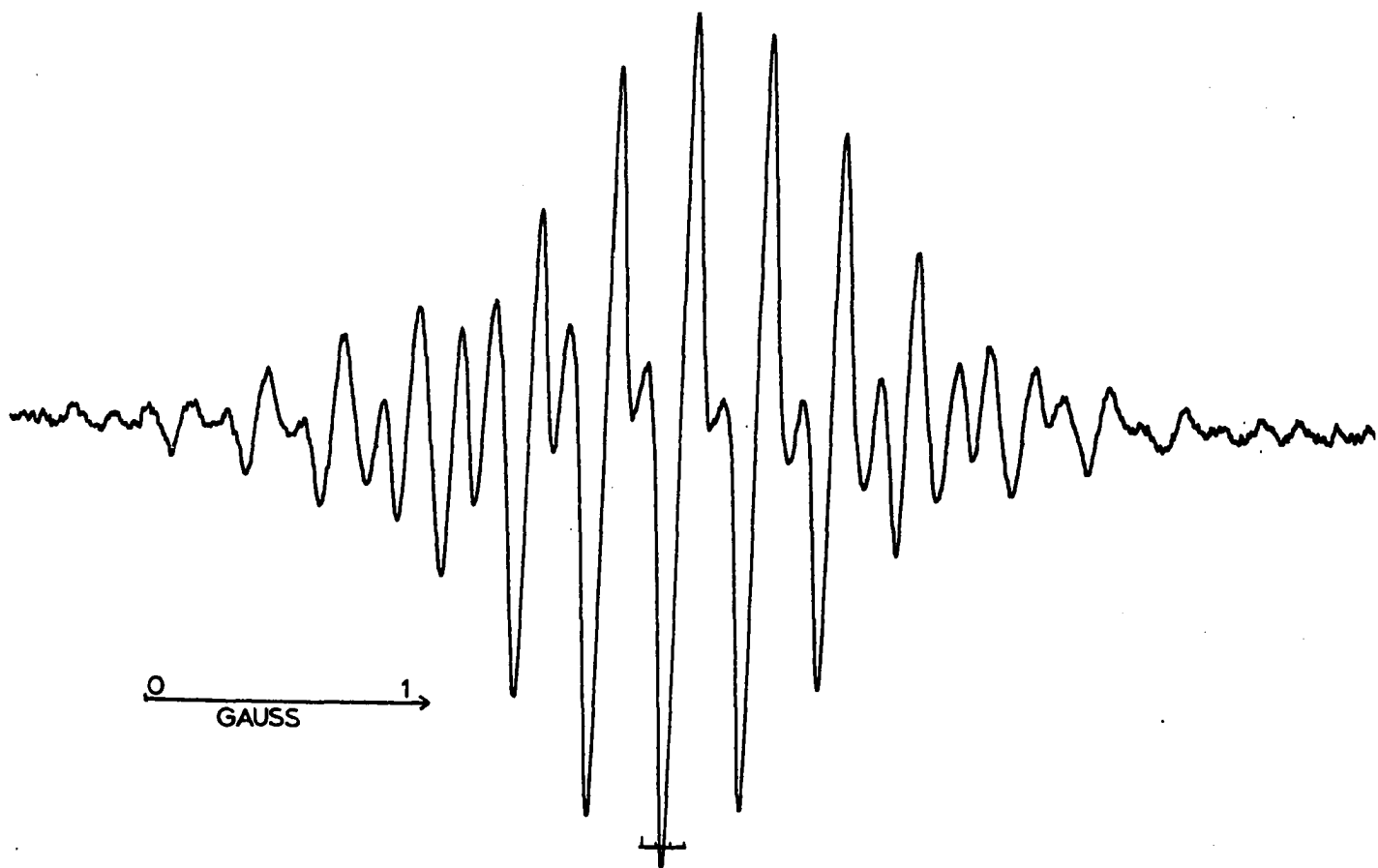
70

A value of -20.9 for  $Q_{C_3C_2}^{C_2}$  has been estimated for the ethyl radical (88). Using this value, equation 70 predicts that  $a^{C_2}$  is negative. Values of  $\rho_{C_3}^{\pi}$ , in light of the large number of approximations made, agree remarkably well with those calculated from equation 68. The experimental value of |4.01| gauss when applied to equation 70, predicts a  $\rho_{C_3}^{\pi}$  of 0.19 as compared to 0.23 for the value of  $a^{C_3}$ . Equation 70 demands that the sign of  $a^{C_2}$  is negative and that an increase in  $|a^{C_2}|$  requires an increase in  $\rho_{C_3}^{\pi}$ . This last prediction is in disagreement with equation 68, and stresses the caution to be exercised in applying the Karplus-Fraenkel equation to  $sp^3$  hybridized carbons. Dimethyl semidione has been prepared by Mr. D. Lawson with  $^{13}C$  at the carbonyl and methyl positions. The observed values for the trans structure of  $a^C$  are 0.5 and 4.5 gauss, respectively. These values correspond to a carbonyl carbon spin density of 0.23 and 0.21 for equations 68 and 70, respectively.

Di-t-butyl acyloin-3- $^{13}C$  was prepared from carbon dioxide- $^{13}C$  and t-butylmagnesium chloride as in the synthesis of diisopropyl acyloin-3- $^{13}C$ . The semidione of the former displayed  $^{13}C$  satellites of 1.41 gauss splitting (Figure 27a).

Figure 27. (a) First-derivative ESR spectrum of di-t-butyl semidione- $\beta$ - $^{13}\text{C}$  (top) in DMSO.

(b) First-derivative ESR spectrum of di-4-heptyl semidione in DMSO displaying natural abundance  $^{13}\text{C}$  splittings. The superimposed spectrum is 10 times the intensity of the original.



Equation 68 predicts a 1.0% increase in the carbonyl carbon  $\rho^{\pi}$  in di-t-butyl semidione over the carbonyl carbon  $\rho^{\pi}$  in dimethyl semidione. This prediction can be tested by synthesizing t-butyl methyl semidione. The methyl group splitting is expected to increase in magnitude from 5.70 gauss and reflect the increased spin density. Carbon-13 hyperfine splitting constants for the tertiary and methyl positions of di-t-butyl semidiones are probably present in natural abundance. However, the complexity of the spectrum makes assignment difficult. Splitting constants of 2.4 and 3.8 gauss have been reported (17).

Table 8 contains  $^{13}\text{C}$  splitting constants for the above compounds. Splitting constants are also tabulated for non-enriched semidiones displaying natural abundance  $^{13}\text{C}$  satellite. Assignments of the carbonyl carbon splittings are based upon the line broadening effects noted above. The other set of splittings are probably due to the  $\alpha$  carbon atom and therefore, are assigned tentatively to this carbon atom. A representative spectrum displaying natural abundance carbon-13 splittings is shown in Figure 27b.

The Karplus-Fraenkel equation can be applied to di-t-butyl ketyl 71.

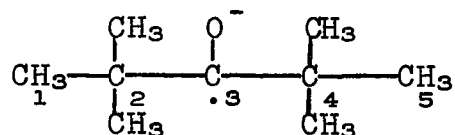


Table 8. Carbon-13 hyperfine splitting constants

Semidione	$a_{\text{carbonyl}}^{\text{C}}$	$ a_{\alpha}^{\text{C}} $
Dimethyl	0.5 <sup>a</sup>	4.5 <sup>a</sup>
Diisopropyl	0.8 <sup>a</sup>	4.0 <sup>a</sup>
Di- <u>t</u> -butyl	1.41 <sup>a</sup>	
Diethyl	$\leq 0.8^{\text{b}}$	4.3 <sup>b</sup>
Cyclohexyl	$\leq 1.0^{\text{b}}$	4.9 <sup>b</sup>
Di- $\beta$ -pentyl	$\leq 1.4^{\text{b}}$	3.55 <sup>b</sup>
Di- $\gamma$ -heptyl	$\leq 1.5^{\text{b}}$	3.45 <sup>b</sup>

<sup>a</sup>Isotopically substituted  $^{13}\text{C}$ .

<sup>b</sup>Natural abundance  $^{13}\text{C}$ .

The basic equation is

$$a_{\text{C}_3}^{\text{C}} = (S^{\text{C}} + 2Q_{\text{C}_3\text{C}_2}^{\text{C}_3} + Q_{\text{C}_3\text{O}}^{\text{C}_3})\rho_{\text{C}_3}^{\pi} + 2Q_{\text{C}_2\text{C}_3}^{\text{C}_3}\rho_{\text{C}_2}^{\pi} + Q_{\text{OC}_3}^{\text{C}_3}\rho_0^{\pi}$$

72

The assumption that  $\rho_{\text{C}_2}^{\pi}$  is negligible becomes severe.

However, there are few methods for estimating  $\rho_{\text{C}_2}^{\pi}$ . Equation 72 with substitution of appropriate  $Q$  values reduces to

$$a_{\text{C}_3}^{\text{C}} = 65 \rho_{\text{C}_3}^{\pi} - 27.1 \rho_0^{\pi}$$

73

The hyperfine splitting constants for oxygen-17 atoms in the radical ions discussed are relatively constant. Typical values for  $a^{\text{O}}$  are -11.1 and -10.5 gauss for di-t-butyl ketyl

and di-t-butyl semidione, respectively. Russell and Underwood (94) have explained these values in terms of constant spin density on oxygen. They argued that using  $Q_{CO}^0 = 0$  and  $Q_O^0 = -40 \pm 5$  (103) for ketyls and semidiones gives a reasonable fit with the  $^{17}O$  hfs. The relationship accounting for the oxygen splitting is given in equation 74.

$$a^0 = Q_O^0 \rho_O^\Pi + Q_{CO}^0 \rho_C^\Pi$$

74

Therefore, using the values 0.25 and 0.75 for  $\rho_O^\Pi$  and  $\rho_{C_3}^\Pi$  in equation 73, a splitting of 42 gauss is predicted for  $a_3^C$ . This estimate is in good agreement with experimental results of 49.6 gauss. Figure 28 shows the spectrum of di-t-butyl ketyl- $\beta$ - $^{13}C$ . Due to the rapidly changing radical concentration, the sign of  $a_3^C$  could not be determined. The Karplus-Fraenkel equation predicts a splitting constant of -16 gauss for  $a_2^C$ . This prediction is not born out by experiment. The spectrum of the ketyl displays only two  $^{13}C$  splittings. The second set of satellites, ( $a^C = 7.6$  gauss) has been assigned to the six methyl carbons on the basis of intensity measurements. However, the same type of experiments have been performed on the ESR spectrum of di-t-butyl nitroxide. One set of  $^{13}C$  satellites was observed ( $a^C = 4.35$  gauss) and was assigned to the methyl carbons (104). Isotopic labelling of the tertiary position betrayed its  $^{13}C$  splitting



Figure 28. First-derivative ESR spectrum of di-t-butyl  
ketyl- $3\text{-}^{13}\text{C}$  in DMSO.



constant. The experimental value of 4.38 gauss differed from the methyl carbon splitting by 0.03 gauss. This small difference was sufficient to invalidate intensity measurements. The same type of fortuitous or nearly fortuitous splitting may be occurring in di-t-butyl ketyl, di-t-butyl semidione and diisopropyl semidione.

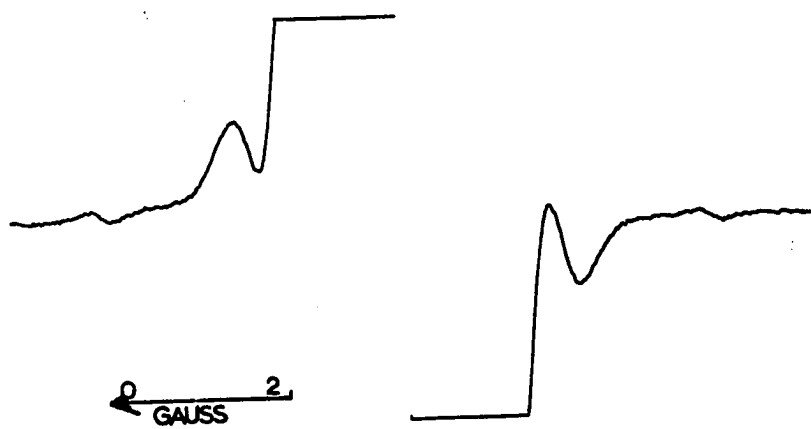
Two sets of satellites have been observed in spectra of concentrated solutions of cyclopropyl semidiones. These lines are apparently due to  $^{13}\text{C}$  in natural abundance. However, the lack of line broadening, uncertain intensity measurements, and the large magnitude of the splittings make assignments difficult. Table 9 contains these splittings. In each case the smaller splitting  $a_1$ , is approximately twice the intensity of the larger splitting  $a_2$ . Figure 29 shows an amplified spectrum of dicyclopropyl semidione displaying two pairs of satellites at 4.5 and 8.1 gauss.

Table 9. Apparent  $^{13}\text{C}$  splittings of cyclopropyl semidiones

Semidione	$a_1^a$ (gauss)	$a_2$ (gauss)
Dicyclopropyl	4.5	8.1
Bis-2,2-dimethylcyclopropyl	4.3	7.95
Di-6-bicyclo[3.1.0]hexyl	8.7	17.5
Di-7-bicyclo[4.1.0]heptyl	8.7	17.4
Di-8-bicyclo[5.1.0]octyl	8.2	16.5
Di-9-bicyclo[6.1.0]nonyl	5.4	9.6

<sup>a</sup>The measured intensity of  $a_1$  is about twice that of  $a_2$ .

Figure 29. First-derivative ESR spectrum of dicyclopropyl semidione in DMSO displaying two sets of apparent  $^{13}\text{C}$  splittings.



## EXPERIMENTAL

## Methods

The ESR spectra in this work were obtained using both a Varian V-4502 spectrometer equipped with a 9 in. magnet and 100 Kcps field modulation and a Varian E-3 spectrometer. Samples were prepared using the H-type mixing cell and a flat-fused silica sample cell. The samples were deoxygenated with a slow stream of prepurified nitrogen that had been passed through successive columns of alkaline pyrogallol and concentrated sulfuric acid. The techniques involved have been previously described (16, 62).

The concentration of dicyclopropyl semidione ions was determined by comparison of peak height of an overmodulated signal of the radical anion with a similarly overmodulated signal from diphenyl picrylhydrazyl (DPPH) ( $1.0 \times 10^{-5}$  molar in benzene). The technique has been described (105).

All IR spectra were obtained in carbon tetrachloride solution using a Perkin-Elmer Model 21 Double Beam Infrared Spectrophotometer. The NMR spectra reported were obtained in carbon tetrachloride containing 1% tetramethylsilane using a Varian A-60 NMR Spectrometer. Gas phase chromatography (GPC) was used to purify many of the compounds studied. Unless otherwise stated, an Aerograph Model A-350-B Dual Column-Temperature Programmer Gas Chromatograph was used with a five foot 15% diethyleneglycolsuccinate on Chromasorb W column.

Purification and Synthesis of  $^{13}\text{C}$  Compounds

The chemicals employed were commercially available products. Dimethyl sulfoxide was distilled from calcium hydride under reduced pressure and stored over molecular sieves in glass stoppered vessels. Xylene was refluxed for twelve hours over sodium and then carefully distilled under a nitrogen atmosphere. The distillate was stored in glass stoppered vessels. Dimethoxyethane was distilled from sodium-potassium alloy and stored in a glass stoppered container. Sodium metal was added to commercial containers of anhydrous ethyl ether (Baker Analyzed Reagent). The ether was then used without further purification.

Dicyclohexyl acyloin

Dicyclohexyl acyloin was prepared by modifying the acyloin condensation procedure of McElvain (106). Cyclohexanecarboxylic acid was heated with thionyl chloride (107). The resulting acid chloride was distilled and treated with absolute ethanol. Ethyl cyclohexanecarboxylate was distilled (b.p.  $193\text{-}194^\circ$ ; lit. (102),  $196^\circ$ ) in 90% yield. To a 500 ml. three-neck flask equipped with a reflux condenser, dropping funnel with side arm and an efficient stirrer, 100 ml. of xylene (54) and 4.6 g. (0.2 moles) of sodium was added. The dropping funnel was charged with 14.3 g. (0.1 moles) of ethyl cyclohexanecarboxylate and a nitrogen inlet. A slow stream of nitrogen was maintained throughout the reaction. The mixture was heated to  $105^\circ\text{-}110^\circ$ , and the ester

added dropwise for one hour with stirring. The stirring was continued for an additional hour, and the reaction was then quenched with 5 ml. of methanol followed by 100 ml. of distilled water. The xylene layer was washed with water, acidified with dilute hydrochloric acid, and neutralized with sodium bicarbonate solution. Distillation of the xylene gave an oil which crystallized in 50/50 ethanol-water to give 5.1 g. of dicyclohexyl acyloin (m.p.,  $43.5^\circ$ ) in 45% yield (109).

Analysis Calc. for  $C_{14}H_{24}O_2$ : C, 74.85; H, 10.76.

Found: C, 74.77; H, 10.65.

Infrared ( $CCl_4$ ) 2.86M, 3.42S, 3.50S, 5.77S, 6.83W, 6.88S, 7.15M, 7.31M, 7.61M, 8.03M, 8.57M, 8.75M, 8.90S, 9.30M, 9.40S, 10.09S (microns).

NMR ( $CCl_4$ ) Doublet centered at 4.01 $\delta$ ,  $^3J_{AB} = 1$  Hz. (total area 1 proton), sharp hydroxyl singlet at 3.20 $\delta$  (area 1 proton), multiplet at 2.20 $\delta$ -2.70 $\delta$  (total area 1 proton), multiplet at 0.90 $\delta$ -2.20 $\delta$  (total area 21 protons).

Mass Spec Mol. wt. 224; found  $M^+$  = 224.



Dicyclopropyl acyloin

To 12.5 g. of sodium in a 100 ml. three-necked flask, equipped with a paddle stirrer, was added 200 ml. xylene. The flask was heated until the sodium melted. The melt was agitated until small particles 1-3 mm. in diameter were formed by manually rotating the paddle stirrer back and forth rapidly (110). The mixture was allowed to cool slowly and the xylene decanted. The sodium sand was washed five times with 100 ml. portions of anhydrous ether. Five hundred ml. of anhydrous ether were added, and the flask was fixed with condenser and dropping funnel as in the synthesis of dicyclohexyl acyloin. The ester, 28.5 g.(0.25 moles), (b.p., 130-132°; lit (111), 133-134°) was dissolved in 100 ml. of ether and added dropwise over the course of one hour to the refluxing mixture. Reflux was maintained for an additional three hours. The unreacted sodium was destroyed by careful addition of water. The ether layer was washed with water and acidified with a 3% hydrochloric acid solution saturated with ammonium chloride to reduce the possibility of ring opening. After neutralizing with saturated sodium bicarbonate solution and drying over anhydrous sodium sulfate, the ether was removed by distillation. The residue was fractionated by GPC on a ten foot silicone 550 column, 155°, gas flow 35 ml./min. using an Aerograph 200 instrument. Dicyclopropyl acyloin has a retention time of six minutes under these

conditions. The acyloin was collected from GPC as an oil.

Analysis Calc. for  $C_8H_{12}O_2$ : C, 68.45; H, 8.62.

Found: C, 68.17; H, 8.80.

Infrared ( $CCl_4$ ) 3.87M, 3.24W, 3.30MW, 3.37M, 3.40M, 3.48MW, 5.90S, 6.15W, 6.87M, 7.27S, 7.40M, 8.07MW, 8.38M, 8.60M, 8.83M, 9.07M, 9.30S, 9.50S, 9.80S (microns).

NMR ( $CCl_4$ ) Doublet centered at 3.93 $\delta$ ,  $^3J_{AB} = 6$  Hz. (total area 1 proton), broad hydroxyl singlet at 3.21 $\delta$  (area 1 proton), multiplet at 1.88 $\delta$ -2.35 $\delta$  (total area 1 proton), multiplet at 0.75 $\delta$ -1.30 $\delta$  (total area 5 protons), multiplet at 0.15 $\delta$ -0.75 $\delta$  (total area 4 protons).

#### Dicyclobutyl acyloin

Ethyl cyclobutanecarboxylate (b.p., 150-151°; lit. (112), 147.5-149° at 746 mm) was prepared by the thionyl chloride esterification procedure (107) in 90% yield. A sample of 23 g. (0.18 moles) of ester was reacted with 8.4 g. (0.36 moles) of sodium sand as in the synthesis of dicyclopropyl acyloin. Work-up yielded 3 g. of a yellow liquid that proved to be a 50/50 mixture of dicyclobutyl acyloin and dicyclobutylethanedione. The mixture was separated by GPC on a ten foot propylene glycol column, 150° flow rate 30 ml./min. in an Aerograph 200. Retention time of the acyloin was 40

minutes, of the diketone, 32 minutes. Total yield of dicyclobutyl acyloin was 1.2 g. (8.6%).

Analysis Calc. for  $C_{10}H_{16}O_2$ : C, 71.30; H, 9.60.

Found: C, 71.25; H, 9.67.

Infrared ( $CCl_4$ ) 2.87M, 3.42S, 3.50S, 5.75W, 5.89S, 6.93M, 7.25M, 7.40S, 8.07M, 8.68M, 8.98S, 9.25M, 9.90M, 10.20S (microns).

NMR ( $CCl_4$ ) Doublet centered at 3.96 $\delta$ ,  $^3J_{AB} = 3.8$  Hz. (total area 1 proton), broad hydroxyl singlet at 3.38 $\delta$  (area 1 proton), multiplet 1.5 $\delta$ -3.2 $\delta$  (total area 14 protons).

#### Dicyclopentyl acyloin

Ethyl cyclopentanecarboxylate (b.p., 65-68° at 13 mm.; lit. (113), 89.3° at 45 mm.) was prepared by thionyl chloride esterification in 85% yield. The acyloin was prepared exactly as dicyclohexylacyloin using 17.8 g. (0.125 moles) of ester and 5.8 g. (0.25 moles) of sodium and 100 ml. of xylene. The residue after evaporating the xylene was a yellow viscous liquid which distilled at 83-87° at 1 mm. to yield 1.0 g. (9% yield) of dicyclopentyl acyloin as an oil.

Analysis Calc. for  $C_{12}H_{20}O_2$ : C, 73.40; H, 10.28.

Found: C, 73.07; H, 10.31.

Infrared ( $CCl_4$ ) 2.86W, 3.42S, 3.49S, 5.87S, 6.88M, 7.23W, 7.36M, 7.70W, 8.18W, 8.60W, 9.25M, 9.35M, 9.75M (microns).

NMR (CCl<sub>4</sub>) Broad singlet 4.89 $\delta$  (area 1 proton), doublet centered at 4.21 $\delta$ ,  $^3J_{AB} = 4$  Hz. (total area 1 proton), multiplet at 2.90 $\delta$ -3.40 $\delta$  (total area 1 proton), multiplet 1.00 $\delta$ -2.90 $\delta$  (total area 17 protons).

Dicycloheptyl acyloin

Ethyl cycloheptanecarboxylate (b.p., 100-102° at 15 mm.; lit. (114), 74° at 3 mm.) was prepared by thionyl chloride esterification (107) in 90% yield. A 17.0 g. (0.10 moles) sample of ester and 5.0 g. of sodium were reacted as in the synthesis of dicyclohexyl acyloin. The residue was distilled. Dicycloheptyl acyloin (b.p., 127-130° at 2 mm.) was collected in 40% yield (5.1 g.).

Analysis Calc. for C<sub>13</sub>H<sub>28</sub>O<sub>2</sub>: C, 76.15; H, 11.18.  
Found: C, 76.40; H, 11.34.

Infrared (CCl<sub>4</sub>) 2.88M, 3.50S, 3.74W, 5.90S, 6.85S, 6.92S, 7.18M, 7.31M, 7.62M, 7.90M, 8.20M, 8.51M, 8.87M, 9.45S (microns).

NMR (CCl<sub>4</sub>) Doublet centered at 4.08 $\delta$ ,  $^3J_{AB} = 1.5$  Hz. (total area 1 proton), broad hydroxyl singlet at 3.75 $\delta$  (area 1 proton), multiplet at 2.00 $\delta$ -3.00 $\delta$  (total area 2 protons), multiplet at 1.00 $\delta$ -2.00 $\delta$  (total area 24 protons).

Mass Spec Mol. wt. 252; found M<sup>+</sup> = 252, M<sup>+</sup>-2 = 250.

Di-4-cycloheptenyl acyloin

4-Cyclopentenecarboxylic acid was prepared by the method of Stork and Landesman (115). The ethyl ester (b.p., 120-125° at 17 mm.) was prepared in 90% yield by the thionyl chloride procedure (107), 12.0 g. (0.078 moles) sample of ester and 3.6 g. (0.15 moles) of sodium were reacted as in the synthesis of dicyclohexyl acyloin. The residue was chromatographed on silica gel. The 80% benzene 20% ether fraction yielded 0.5 g. of a yellow oil (5.1%).

Analysis Calc. for  $C_{16}H_{24}O_2$ : C, 77.23; H, 9.51.

Found: C, 76.55; H, 9.65.

Infrared ( $CCl_4$ ) 2.87M, 2.31M, 3.50S, 5.50W, 5.85S, 6.05M, 6.94S, 7.15M, 7.30M, 7.65M, 8.20M, 8.80M, 9.30S, 9.75S (microns).

NMR ( $CCl_4$ ) Multiplet at 5.6-5.8 (total area 4 protons), doublet centered at 4.11 $\delta$ ,  $^3J_{AB} = 2.4$  Hz. (total area 1 proton).

Mass Spec Mol. wt. 248; found  $M^+$  = 248.

Cyclopropyl methyl acyloin

Sodium sand, 35 g. (1.5 moles) was prepared in a 1000 ml. three-necked flask. The flask was fitted with a condenser and a dropping funnel as in the preparation of dicyclohexyl acyloin. The flask was flushed with nitrogen, charged with 500 ml. ether, and heated to reflux with vigorous stirring.

A solution of 28.5 g. (0.25 moles) of ethyl cyclopropane-carboxylate and 50 ml. (0.50 moles) of ethyl acetate dissolved in 100 ml. of ether was added dropwise for one hour. The nitrogen flow, stirring, and refluxing were maintained for sixteen hours. The reaction mixture was worked up as in the procedure for dicyclopropyl acyloin. The resulting solution was carefully heated under 15 mm. pressure until 35°C. The distillate contained unreacted ester and acetoin. The residue was separated by GPC on a five foot silicone 550 column in an Aerograph 220 instrument. A column temperature of 200°C. yielded a 17 peak chromatograph. The peaks were divided into three parts, and fractions were collected and analysed by ESR. The first fraction (2.0 min.) displayed a five line spectrum indicating the presence of both cyclopropyl methyl acyloin and dicyclopropyl acyloin. The second fraction (2.0 min./8 min.) displayed a singlet for dicyclopropyl acyloin, and the third fraction gave only a weak unidentifiable singlet. The column temperature was lowered to 135°, and the first fraction was separated further into twelve peaks. The chromatograph was divided into four parts. The second fraction was the largest peak and upon ESR analysis proved to be cyclopropyl methyl acyloin. Total yield was 0.10 g. (0.4%) colorless liquid.

Analysis      Calc. for  $C_6H_{10}O_2$ : C, 63.08; H, 8.85.

Found: C, 63.02; H, 8.72.

Infrared (CCl<sub>4</sub>) 2.95W, 3.40M, 3.48M, 5.80S, 6.15W, 6.84M, 7.10M, 7.25S, 7.95M, 8.15M, 8.33S, 8.55S, 9.14M, 9.40M (microns).

NMR (CCl<sub>4</sub>) Quartet centered at 4.29 $\delta$ ,  $^3J_{AB} = 7$  Hz. (total area 1 proton, broad hydroxyl singlet at 4.05 $\delta$  (area 1 proton), small singlet at 2.21 $\delta$  and a large doublet centered at 1.37 $\delta$ ,  $^3J_{AB} = 7$  Hz. (total area 3 protons), multiplet from 0.20 $\delta$ -2.16 $\delta$  (total area 5 protons)).

Cyclobutyl methyl acyloin

A 0.25 mole sample of ethyl cyclobutanecarboxylate and 1.00 moles of ethyl acetate were reacted with sodium sand as in the synthesis of cyclopropyl methyl acyloin. Exhaustive GPC analysis combined with ESR detection of the acyloin yielded 0.2 g. (1.0%) of cyclobutyl methyl acyloin as an oil.

Analysis Calc. for C<sub>7</sub>H<sub>12</sub>O<sub>2</sub>: C, 65.60; H, 9.45.  
Found: C, 65.19; H, 9.41.

Infrared (CCl<sub>4</sub>) 2.95S, 3.42S, 3.49S, 5.85S, 6.88M, 7.28S, 8.00M, 8.22M, 8.92S, 9.00S (microns).

NMR (CCl<sub>4</sub>) Multiplet 3.35 $\delta$ -3.80 $\delta$  (total area 1 proton), broad hydroxyl singlet at 3.33 $\delta$  (area 1 proton), small singlet at 2.00 $\delta$  and a large doublet centered at 1.15 $\delta$ ,  $^3J_{AB} = 5.5$  Hz. (total area 3 protons), multiplet

at 1.60 $\delta$ -2.10 $\delta$  (total area 7 protons).

Cyclopentyl methyl acyloin

Cyclopentanecarboxaldehyde was obtained by the method of Kinstle (116). A 17.8 (0.12 moles) sample of cyclopentyl bromide was reacted with 3 g. magnesium turnings in 300 ml. ether to produce the Grignard reagent. The reaction flask was cooled to 15°C., and 13.3 g. (0.09 moles) freshly distilled triethyl orthoformate in 150 ml. ether was added during five minutes. The reaction mixture was stirred and heated under reflux for five hours, and the bulk of the ether was removed by careful distillation. A mild exothermic reaction occurred and was controlled by an ice salt bath. The grey paste remaining was dispersed in 75 ml. water and neutralized with a small amount of hydrochloric acid. The aldehyde was extracted with three 50 ml. portions of ether. The ether solution was dried and evaporated to yield a yellow oil. Saturated sodium bisulfite solution was then added and the mixture stirred overnight. The sodium bisulfite addition product was collected on a sintered glass funnel and washed with two 50 ml. portions of ethanol, three 50 ml. portions of ether and then dried. The adduct weighing 37.2 g. was added to 12.5 g. of sodium cyanide dissolved in 25 ml. of water. The solution was stirred with 10 ml. of ether for two hours and extracted with three 25 ml. portions of ether. The combined ether extract was dried over anhydrous magnesium sulfate. Methylmagnesium iodide was prepared in a 1000 ml.,



three-necked flask from 28.0 g. (0.20 moles) methyl iodide and 5.0 g. of magnesium turnings in 500 ml. ether. After refluxing the Grignard reagent for four hours, the ether solution of cyclopentanecarboxaldehyde cyanohydrin was added dropwise during the course of one hour (117). The mixture was heated under reflux for an additional four hours and then cooled in an ice-methanol bath. Water was added cautiously until two distinct layers formed, and hydrochloric acid was added until the basic salts dissolved. The mixture was extracted with three 50 ml. portions of ether. The combined ether extract was washed with saturated sodium bicarbonate and then dried over anhydrous sodium sulfate. The ether was removed by careful distillation and the residue distilled on a vacuum line. A 5.0 g. (28.2%) fraction (b.p., 25-26° at 0.13 mm.) of cyclopentyl methyl acyloin was collected.

Analysis Calc. for  $C_8H_{14}O_2$ : C, 67.50; H, 9.93.

Found: C, 67.42; H, 10.06.

Infrared ( $CCl_4$ ) 2.85M, 3.39S, 3.48S, 5.85S, 6.89M, 7.20M, 7.37S, 7.70W, 8.07M, 8.70M, 9.02S, 9.35M, 9.75M (microns).

NMR ( $CCl_4$ ) Multiplet at 3.95 $\delta$ -4.20 $\delta$  (total area 1 proton), broad hydroxyl singlet at 3.20 $\delta$  (area 1 proton), singlet at 2.11 $\delta$  and a doublet centered at 1.30 $\delta$ ,  $^3J_{AB} = 7$  Hz. (total area 3 protons), multiplet at 1.20 $\delta$ -

2.00 $\delta$  (total area 9 protons).

Cyclohexyl methyl acyloin

A 10 g. sample of cyclohexanecarboxaldehyde was added to 50 ml. of saturated sodium bisulfite. The mixture was stirred overnight and then filtered. The filtrate was washed with two 50 ml. portions of ethanol and three 50 ml. portions of ether and then dried. The cyclohexanecarboxaldehyde-sodium bisulfite addition product (20.93 g.) was added to 6.86 g. (0.14 moles) of sodium cyanide dissolved in 25 ml. of water. The mixture was treated as in the synthesis of cyclopentyl methyl acyloin yielding 5 g. (40.5%) cyclohexanecarboxaldehyde cyanohydrin. The cyanohydrin was reacted with 0.08 moles of methylmagnesium iodide to produce 1.2 g. (19.9% yield) of cyclohexyl methyl acyloin (b.p. 100-110° at 13 mm.).

Analysis Calc. for C<sub>9</sub>H<sub>16</sub>O<sub>2</sub>: C, 69.30; H, 10.30.

Found: C, 69.64; H, 10.13.

Infrared (CCl<sub>4</sub>) 2.95W, 3.41S, 3.50S, 5.80M, 5.85S, 6.89S, 7.28M, 8.05M, 8.45M, 9.00M, 9.43S, 9.70M (microns).

NMR (CCl<sub>4</sub>) Multiplet at 3.30 $\delta$ -3.63 $\delta$  (total area 1 proton), broad hydroxyl singlet at 2.15 $\delta$  (area 1 proton), small singlet at 1.96 $\delta$  and a large doublet centered at 1.10 $\delta$ ,  $^3J_{AB}$  = 6.25 Hz. (total area 3 protons), multiplet at 0.90 $\delta$ -2.10 $\delta$  (total area 11 protons).

Cyclooctyl methyl acyloin

A 10 g. sample of cyclooctanecarboxaldehyde was treated as in the synthesis of cyclohexyl methyl acyloin to yield 2.1 g. (16.1%) of cyclooctyl methyl acyloin. The acyloin was purified by GPC and isolated as an oil.

Analysis Calc. for  $C_{11}H_{20}O_2$ : C, 71.75; H, 10.87.

Found: C, 71.37; H, 11.25.

Infrared ( $CCl_4$ ) 2.87W, 3.39S, 3.48S, 5.87S, 6.88M, 7.79M, 7.70W, 8.57W, 9.30M, 9.76M (microns).

NMR ( $CCl_4$ ) Doublet centered at 4.06 $\delta$ ,  $^3J_{AB} = 3.5$  Hz. (total area 1 proton), broad hydroxyl singlet at 3.26 $\delta$  (area 1 proton), large singlet at 2.12 $\delta$  and small doublet centered at 1.12 $\delta$ ,  $^3J_{AB} = 6.25$  Hz. (total area 3 protons), multiplet at 1.0 $\delta$ -2.5 $\delta$  (total area 15 protons).

Mass Spec Mol. wt. 184, found  $M^+ = 184$ .

Di-7-bicyclo[4.1.0]heptyl acyloin

Ethyl 7-norcaranecarboxylate was synthesized by modifying the method of Ebel, Brunner, and Mangelli (118). Zinc-copper catalyst was prepared using the method of Shank and Shechter (119). A 1000 ml. three-necked flask was fitted with condenser, paddle stirrer and dropping funnel as in the synthesis of dicyclohexyl acyloin. A 15 g. sample of zinc-copper catalyst was suspended in 350 g. of cyclohexene and

heated to reflux. The mixture was stirred as 100 g. of ethyl diazoacetate was added dropwise for three hours. Refluxing temperature was maintained for an additional 12 hours. The solution was filtered and distilled at aspirator pressure. The fraction distilling at 107-110°C. at 15 mm. was collected. GPC analysis showed the presence of three compounds: ethyl-7-norcaranecarboxylate, diethyl maleate, and diethyl fumarate. The mixture was separated by saponification of 32.4 g. of crude ester with 200 ml. of 10% sodium hydroxide. The resultant clear yellow solution was washed with two 50 ml. portions of ether and acidified with hydrochloric acid. The precipitate was collected on a medium porosity sintered glass filter and washed with five 100 ml. portions of water. The crude acid (m.p. 94-96°, lit. (120) 97-98°) was dried under aspirator pressure for five hours. Total yield of norcaranecarboxylic acid was 19.2 g. This was treated to yield 21.4 g. of 7-norcaranecarboxylic acid chloride (b.p., 102-104° at 15 mm., lit. (120) 112°, 25 mm.). The acid chloride was converted to the ethyl ester (b.p. 107-108° at 15 mm., lit. (118) 108-110° at 18 mm.) in 95% yield. Total yield of ester based on ethyl diazoacetate was 16%. An 11.3 g. (0.065 moles) sample of freshly distilled ester was reacted with 3.0 g. of sodium in 100 ml. of xylene as in the synthesis of dicyclohexyl acyloin. Pure di-7-bicyclo-[4.1.0]heptyl acyloin was distilled at 135°, at 0.03 mm. Total

yield was 1.5 g. (35%).

Analysis Calc. for  $C_{16}H_{24}O_2$ : C, 77.25; H, 9.74.

Found: C, 77.23; H, 9.57.

Infrared ( $CCl_4$ ) 2.90W, 3.42S, 3.50S, 5.94S, 6.90M, 7.06M, 3.43M, 7.67M, 8.67M, 9.07M, 9.30M, 9.50M (microns).

NMR ( $CCl_4$ ) Broad hydroxyl singlet at 3.28 $\delta$  (area 1 proton), doublet centered at 3.35 $\delta$ ,  $^3J_{AB} = 6.7$  Hz. (total area 1 proton), multiplet at 0.50 $\delta$ -2.30 $\delta$  (total area 22 protons).

Ethyl-6-bicyclo[3.1.0]hexanecarboxylate

A 200 g. sample of cyclopentene was treated with 100 g. of ethyl diazoacetate as in the synthesis of di-7-bicyclo-[4.1.0]heptyl acyloin to yield 10.10 g. (8.0%) of 6-bicyclo-[3.1.0]hexanecarboxylic acid chloride (b.p. 79-80° at 15 mm., lit. (121,122). The ethyl ester (b.p. 89° at 15 mm.) was formed by addition of ethanol to acid chloride in 95% yield (121).

Analysis Calc. for  $C_9H_{14}O_2$ : C, 70.10; H, 9.15.

Found: C, 69.70; H, 8.99.

Infrared ( $CCl_4$ ) 3.42M, 3.52W, 5.81VS, 6.90W, 7.09M, 7.22W, 7.33W, 7.54M, 7.70W, 7.91S, 8.16W, 8.58VS, 9.26M, 9.33M, 9.54M, 9.81W (microns).

NMR ( $CCl_4$ ) Quartet centered at 4.02 $\delta$ ,  $^3J_{AB} = 7.1$  Hz. (total area 2 protons), multiplet at 1.66 $\delta$ -2.05 $\delta$  (total area 6 protons), triplet

centered at 1.21 $\delta$ ,  $^3J_{AB} = 7.1$  Hz. (total area 3 protons), multiplet at 0.90 $\delta$ -1.60 $\delta$  (total area 3 protons).

Di-6-bicyclo[3.1.0]hexyl acyloin

A 9.77 g. (0.064 moles) sample of ethyl 6-bicyclo[3.1.0]-hexanecarboxylate was reacted with 3 g. sodium as in the synthesis of dicyclohexyl acyloin to yield 0.5 g. (6.2%) of di-6-bicyclo[3.1.0]hexyl acyloin. The acyloin was purified by distillation in a Tepler still at 0.05 mm. and was collected as an oil.

Analysis Calc. for  $C_{14}H_{20}O_2$ : C, 76.37; H, 9.23.

Found: C, 76.55; H, 9.34.

Infrared ( $CCl_4$ ) 2.90W, 3.42S, 3.50S, 5.94S, 6.90M, 7.20M, 7.55M, 7.72M, 7.90M, 8.16M, 8.52M, 9.15M, 9.34M, 9.50M (microns).

NMR ( $CCl_4$ ) Broad hydroxyl singlet at 5.40 $\delta$  (area 1 proton), doublet centered at 3.66 $\delta$ ,  $^3J_{AB} = 8$  Hz. (total area 1 proton), multiplet 0.7 $\delta$ -3.20 $\delta$  (total area 18 protons).

Ethyl 8-bicyclo[5.1.0]octanecarboxylate

A 120 g. sample of freshly distilled cycloheptene was treated with 7.5 g. of zinc-copper catalyst and 50 g. of ethyl diazoacetate as in the synthesis of di-7-bicyclo[4.1.0]-heptyl acyloin to yield 11.1 g. (14.4%) of bicyclo[5.1.0]-octanecarboxylic acid chloride (b.p. 115-116° at 15 mm.).

The ethyl ester (b.p. 138-141° at 15 mm.) was formed by addition of ethanol to the acid chloride in 90% yield.

Analysis Calc. for  $C_{11}H_{18}O_2$ : C, 72.48; H, 9.96.

Found: C, 72.51; H, 9.88.

Infrared ( $CCl_4$ ) 3.35W, 3.42S, 3.51M, 5.80VS, 6.75W, 6.83S, 6.94M, 7.30M, 7.44M, 7.61S, 7.92M, 8.23MS, 8.57VS, 8.87M, 9.13M, 9.45W, 9.72M (microns).

NMR ( $CCl_4$ ) Quartet centered at 4.02 $\delta$ ,  $^3J_{AB} = 7$  Hz. (total area 2 protons), triplet centered at 1.20 $\delta$ ,  $^3J_{AB} = 7$  Hz. (total area 3 protons), multiplet at 0.80 $\delta$ -2.45 $\delta$  (total area 13 protons).

Di-8-bicyclo[5.1.0]octyl acyloin

A 10.2 g. (0.054 moles) sample of ethyl 8-bicyclo[5.1.0]-octylcarboxylate was reacted with 2.73 g. of sodium as in the synthesis of dicyclohexyl acyloin to yield 1.5 g. (21.6%) of di-8-bicyclo[5.1.0]octyl acyloin. The acyloin was purified by distillation in a Tepler still at 0.05 mm. and was collected as a viscous oil.

Analysis Calc. for  $C_{18}H_{28}O_2$ : C, 78.21; H, 10.21.

Found: C, 78.29; H, 10.17.

Infrared ( $CCl_4$ ) 2.95W, 3.44S, 3.50S, 5.94S, 6.50M, 6.90M, 7.42M, 7.65M, 7.82M, 8.25M, 8.45M, 8.80M, 9.40M (microns).

NMR (CCl<sub>4</sub>) Broad hydroxyl singlet 4.52δ  
(total area 1 proton), broad multiplet 0.50δ-  
3.0δ (total area 27 protons).

Ethyl 9-bicyclo[6.1.0]nonanecarboxylate

A 200 g. sample of cyclooctene was treated with 50 g. of ethyl diazoacetate as in the synthesis of di-7-bicyclo[4.1.0]-heptyl acyloin to yield 9.85 g. (10.0%) of 9-bicyclo[6.1.0]-nonanecarboxylic acid chloride (b.p. 140-141° at 15 mm.). The ethyl ester (b.p. 143.5-144.5° at 18 mm., lit.(123) 100-105° at 3 mm.) was formed by addition of ethanol to the acid chloride in 95% yield.

Analysis Calc. for C<sub>12</sub>H<sub>20</sub>O<sub>2</sub>: C, 73.45; H, 10.28.

Found: C, 73.25; H, 10.38.

Infrared (CCl<sub>4</sub>) 3.33W, 3.40S, 3.49M, 5.78VS, 6.79M, 6.85W, 6.89M, 6.95W, 7.28M, 7.41M, 7.47W, 7.59S, 7.68M, 7.84M, 8.16M, 8.26M, 8.40S, 8.49VS, 8.71VS, 9.12W, 9.37W, 9.82M (microns).

NMR (CCl<sub>4</sub>) Quartet centered at 4.03δ, <sup>3</sup>J<sub>AB</sub> = 7.2 Hz. (total area 2 protons), triplet centered at 1.20δ, <sup>3</sup>J<sub>AB</sub> = 7.2 Hz. (total area 3 protons), multiplet at 0.85δ-2.25δ (total area 15 protons).

Di-9-bicyclo[6.1.0]nonyl acyloin

A 9.57 g. (0.049 moles) sample of ethyl 9-bicyclo[6.1.0]nonanecarboxylate was reacted with 2.3 g. (0.1 moles) of sodium as in the synthesis of dicyclohexyl acyloin to yield



0.5 g. (6.5%) of di-9-bicyclo[6.1.0]nonyl acyloin. The acyloin was purified by distillation in a Tepler still at 0.03 mm. and was collected as viscous oil.

Analysis Calc. for  $C_{20}H_{32}O_2$ : C, 78.90; H, 10.59.

Found: C, 78.88; H, 10.36.

Infrared ( $CCl_4$ ) 2.90W, 3.45S, 3.52S, 5.95S, 6.83M, 6.93M, 7.25W, 7.45M, 7.63M, 8.64M, 9.04M, 9.36M (microns).

NMR ( $CCl_4$ ) Doublet centered at 3.78 $\delta$ ,  $^3J_{AB} = 7$  Hz. (total area 1 proton), broad hydroxyl singlet at 3.28 $\delta$  (area 1 proton), multiplet at 0.50 $\delta$ -3.2 $\delta$  (total area 28 protons).

7-Bicyclo[4.1.0]heptyl methyl acyloin

A 9.2 g. (0.058 moles) sample of freshly distilled 7-norcaranecarboxylic acid chloride was added dropwise to a cool ( $-5^\circ$ ) solution of 2.5 g. (0.058 moles) ethylenimine and 5.9 g. (0.058 moles) triethylamine in 50 ml. of ether (124). The solution was stirred for an hour at  $0^\circ$  and an additional four hours at room temperature ( $28^\circ$ ), then filtered. The amine chloride precipitate was washed with two 50 ml. portions of ether. The combined ether extract was reduced to 50 ml. by distillation and dried overnight with anhydrous magnesium sulfate. The amide solution was filtered and cooled to  $-5^\circ$ . A solution of 2.0 g. (60% excess) of lithium aluminum hydride in 70 ml. ether was added dropwise for 45

minutes. The solution was allowed to reach room temperature and then heated under reflux for three hours. Water was slowly added to destroy the lithium complex. Then 3N hydrochloric acid saturated with ammonium chloride was added until the white solids were dissolved. The mixture was extracted with four 50 ml. portions of ether. The combined ether solution was washed with sodium bicarbonate solution and dried over anhydrous magnesium sulfate. The solution was reduced to 20 ml. by distillation and added to 50 ml. of saturated sodium bisulfite solution. The sodium bisulfite addition product was washed with ether and treated as in the synthesis of cyclohexyl methyl acyloin to yield 0.41 g. (4.2%) of 7-bicyclo[4.1.0]heptyl methyl acyloin. The acyloin was purified by GPC and isolated as an oil.

Analysis Calc. for  $C_{10}H_{26}O_2$ : C, 71.30; H, 9.59.

Found: C, 71.40; H, 9.70.

Infrared ( $CCl_4$ ) 2.93W, 3.44S, 3.51S, 3.70W, 5.85S, 6.90S, 7.10M, 7.40M, 8.04M, 8.55M, 8.95M, 9.30M, 9.69M, 9.80M, 10.90S (microns).

NMR ( $CCl_4$ ) Broad hydroxyl singlet 5.3 $\delta$  (area 1 proton), broad multiplet 0.20 $\delta$ -2.8 $\delta$  (total area 14 protons).

Mass Spec Mol. wt. 168; found  $M^+$  = 168,  $M^+-2$  = 166.

Bis-2,2-dimethylcyclopropyl acyloin

2,2-Dimethylcyclopropyl nitrile (b.p. 150-152°, lit. (125))

154.5-155.5°) was prepared in 60% yield by the method of Nelson et al. The nitrile was hydrolyzed in refluxing potassium hydroxide solution in 20% yield. The resulting acid (b.p. 110° at 15 mm., lit. 125) 198-201°, was esterified via the thionyl chloride procedure to yield ethyl 2,2-dimethylcyclopropanecarboxylate (b.p. 152-155°, lit. (126, 90° at 15 mm.) in 90% yield. A 6.0 g. (0.04 moles) sample of ester was reacted with 3 g. of sodium sand as in the synthesis of dicyclopropyl acyloin. Bis-2,2-dimethylcyclopropyl acyloin was isolated by distillation (b.p. 50-55° at 0.05 mm.) and purified by column chromatography (0.5 g., 12.5%).

Analysis Calc. for  $C_{12}H_{20}O_2$ : C, 73.45; H, 10.28.

Found: C, 73.33; H, 10.11.

Infrared ( $CCl_4$ ) 2.89W, 3.41S, 3.49S, 5.75W, 5.92S, 6.90M, 7.20S, 7.27S, 7.35M, 8.75M, 9.00M, 9.17M, 9.80S (microns).

NMR ( $CCl_4$ ) Broad hydroxyl singlet at 3.72 $\delta$  (area 1 proton), doublet centered at 3.62 $\delta$ ,  $^3J_{AB} = 5.5$  Hz. (total area 1 proton), multiplet at 1.17 $\delta$ -1.26 $\delta$  (total area 6 protons), singlet at 1.10 $\delta$  (total area 6 protons), multiplet 0.30 $\delta$ -2.3 $\delta$  (total area 6 protons).

Mass Spec Mol. wt. 192; found  $M^+$  = 192.

2,2-Dimethylcyclopropyl methyl acyloin

2,2-Dimethylcyclopropyl methyl acyloin was prepared from 13.2 g. (0.10 moles) of 2,2-dimethylcyclopropanecarboxylic acid chloride as in the synthesis of 7-bicyclo[4.1.0]heptyl methyl acyloin. The 0.70 g. (5%) of acyloin obtained was purified by GPC and collected as an oil.

Analysis Calc. for  $C_8H_{14}O_2$ : C, 67.60; H, 9.94.

Found: C, 67.40; H, 10.01.

Infrared ( $CCl_4$ ) 2.87M, 3.40S, 3.48S, 5.83VS, 5.91VS, 6.90S, 7.30VS, 8.05M, 8.65M, 9.00VS, 9.15VS, 9.28VS, 9.69VS, 9.82S (microns).

NMR ( $CCl_4$ ) Multiplet at 4.50 $\delta$ -3.80 $\delta$  (total area 1 proton), broad hydroxyl singlet at 3.35 $\delta$  (area 1 proton), singlet at 2.20 $\delta$  and a doublet centered at 1.35 $\delta$ ,  $^3J_{AB} = 7$  Hz. (total area 3 protons), doublet centered at 1.21 $\delta$ ,  $^3J_{AB} = 1.5$  Hz. (total area 3 protons), doublet centered at 1.09 $\delta$ ,  $^3J_{AB} = 3.0$  Hz. (total area 3 protons), multiplet at 0.30 $\delta$ -2.0 $\delta$  (total area 3 protons).

Mass Spec Mol. wt. 142; found  $M^+ = 142$ ,  $M^+-2 = 140$ .

Isobutyroin(diisopropyl acyloin)

Isobutyroin was prepared by two methods. The first is a modification of the acyloin condensation and gave improved yield in small scale reactions. The second procedure is a

Grignard addition to a cyanohydrin (117,127,128) and was used to prepare isobutyroin from 2-chloropropane.

Method 1. A 1.2 g. (0.052 moles) sample of sodium was converted to sodium sand in a three-necked 50 ml. flask. The flask was fitted with a syringe needle adapter, a nitrogen inlet, a reflux condenser and a magnetic stirrer. The sodium sand was covered with 50 ml. of ether, and the system was flushed with nitrogen. A 5.62 g. (0.052 moles) portion of trimethylchlorosilane (129) was added via syringe. The mixture was stirred and heated under reflux. Freshly distilled ethyl isobutyrate (b.p. 110-111°; lit. (130) 111.7°) (3.0 g., 0.259 moles) was added slowly over 30-45 minutes and the solution refluxed for an additional hour. The sodium chloride formed was filtered and washed with two 10 ml. portions of ether. The combined ether solution was reduced by distillation to 10 ml., and 0.9 ml. of 1N hydrochloric acid was added. The mixture was heated under reflux for two hours. The water layer was separated with a syringe, and 2 g. of calcium carbonate were added. The mixture was brought to reflux for three additional hours. Distillation yielded 1.0 g. (53.8%) of isobutyroin (b.p., 73° at 15 mm.; lit. (131) 66-70° at 12-13 mm).

Method 2. Isobutyraldehyde cyanohydrin (b.p., 106° at 15 mm.; lit. (132) 106-106.5° at 22 mm.) was prepared using the hydrocyanation procedure of Glattefeld and Hoen (133) A 3 g. (0.0382 moles) sample of 2-chloropropane was converted

to isopropylmagnesium chloride with 1.75 g. magnesium turnings in 25 ml. of ether. The apparatus used was the same as in method 1. A syringe was used to add 1.6 g. (0.016 moles) of isobutyraldehyde cyanohydrin slowly to the Grignard. The mixture was heated under reflux for two hours and worked up as in the synthesis of cyclohexyl methyl acyloin. Isobutyroin (0.97 g., 50%) was purified by distillation.

Isovaleroin(diisobutyl acyloin)

Isovaleroin was synthesized using the same procedure as in the synthesis of dicyclohexyl acyloin. Freshly distilled ethyl isovalerate (b.p. 133-135°; lit(134), 135°) was used to prepare the acyloin (b.p. 98-100° at 45 mm.; lit (131) 94-97° at 12-13 mm.) in 62% yield.

3,6-Diethylbutyroin(di-3-pentyl acyloin)

3,6-Diethylbutyroin was synthesized from freshly distilled ethyl 2-ethylbutyrate (b.p. 150°, lit.(135), 151°) using the same procedure as in the synthesis of dicyclohexyl acyloin. The acyloin (b.p., 107-110° at 15 mm.) was distilled in 10% yield and was purified by GPC.

Analysis Calc. for  $C_{12}H_{24}O_2$ : C, 71.98; H, 11.98.

Found: C, 72.41; H, 11.70.

Infrared ( $CCl_4$ ) 2.88W, 3.90S, 3.98S, 5.88S, 6.85S, 7.25M, 7.35W, 8.00W, 8.75M, 8.97M, 9.43M, 9.59M, 9.87M (microns).

NMR ( $CCl_4$ ) Broad hydroxyl peak at 4.2 $\delta$  (area 1 proton), doublet centered at 3.95 $\delta$ ,  $^3J_{AB} =$

4.5 Hz. (total area 1 proton), pentet centered at 2.60 $\delta$ ,  $^3J_{AB} = 6.25$  Hz. (total area 1 proton), multiplet at 0.70 $\delta$ -1.75 $\delta$  (total area 21 protons).

Mass Spec Mol. wt. 200; found  $M^+ = 200$ ,  $M^+-2 = 198$ .

4,7-Dipropylvaleroïn(di-4-heptyl acyloïn)

4,7-Dipropylvaleroïn was synthesized from freshly distilled ethyl 2 propyl valerate (b.p., 111° at 25 mm., lit. (136), 76-78° at 13 mm.) as in the synthesis of dicyclohexyl acyloïn. The acyloïn (b.p. 120° at 15 mm.) was distilled in 70% yield and purified by GPC.

Analysis Calc. for  $C_{16}H_{32}O_2$ : C, 75.24; H, 12.62.

Found: C, 74.94; H, 12.36.

Infrared ( $CCl_4$ ) 2.87W, 3.41S, 3.48S, 5.88S, 6.22W, 6.82S, 7.25M, 7.50W, 8.05W, 9.00W, 9.69M (microns).

NMR ( $CCl_4$ ) Singlet at 4.15 $\delta$  (area 1 proton), broad hydroxyl singlet at 3.10 $\delta$  (area 1 proton, multiplet at 2.20 $\delta$ -3.0 $\delta$  (total area 1 proton), multiplet 0.63 $\delta$ -2.20 $\delta$  (total area 29 protons).

Mass Spec Mol. wt. 256; found  $M^+ = 256$ ,  $M^+-2 = 254$ .

Pivaloïn(di-t-butyl acyloïn)

Pivaloïn was synthesized from freshly distilled ethyl pivalate (b.p. 117-118°; lit. (137), 118-118.2°) as in the

synthesis of dicyclohexyl acyloin. The acyloin (m.p. 78°; lit. (110), 81°) was recrystallized in 58% yield and purified by sublimation.

2-Methyl-4-hydroxy-5-hepten-3-one

Crotonaldehyde cyanohydrin was synthesized using the hydrocyanation procedure of Glatterfeld and Hoen (133). 2-Methyl-4-hydroxy-5-hepten-3-one was prepared by addition of crotonaldehyde cyanohydrin to isopropylmagnesium chloride in 18% yield. The acyloin was purified by GPC and collected as a colorless oil.

Analysis Calc. for  $C_8H_{14}O_2$ : C, 67.60; H, 9.94.

Found: C, 67.61; H, 9.76.

Infrared ( $CCl_4$ ) 2.88W, 3.38M, 3.49M, 5.85S, 5.90S, 6.00VW, 6.10VW, 6.81M, 6.91M, 7.23M, 7.41W, 8.08W, 8.26W, 8.90S, 9.12S, 9.65M, 9.95M, 10.37S (microns).

NMR ( $CCl_4$ ) Multiplet at 5.08 $\delta$ -6.18 $\delta$  (total area 2 protons), doublet of doublets centered at 4.57 $\delta$ ,  $^3J_{AB} = 7$  Hz.,  $^4J_{AB} = 1$  Hz. (total area 1 proton), broad hydroxyl singlet at 4.10 $\delta$  (area 1 proton), heptet centered at 2.88 $\delta$ ,  $^3J_{AB} = 7$  Hz. (total area 1 proton), doublet of doublets centered at 1.75 $\delta$ ,  $^3J_{AB} = 6$  Hz.,  $^4J_{AB} = 1$  Hz. (total area 3 protons), doublet centered at 1.10 $\delta$ ,  $^3J_{AB} = 7$  Hz. (total area 3 protons), doublet centered at 1.05 $\delta$ ,



${}^3J_{AB} = 7 \text{ Hz. (total area 3 protons).}$

Mass Spec Mol. wt. 142; found  $M^+ = 142$ .

Isopropyl propyl acyloin

Isopropyl propyl acyloin was prepared by addition of isobutyraldehyde cyanohydrin to *n*-propylmagnesium bromide in 70% yield. The acyloin (b.p. 75-77° at 15 mm.) was purified by GPC.

Analysis Calc. for  $C_8H_{16}O_2$ : C, 66.68; H, 11.19.

Found: C, 66.78; H, 11.27

Infrared ( $CCl_4$ ) 2.88M, 3.40-3.50S, 5.70W, 5.86S, 6.84S, 7.22S, 7.32S, 7.78M, 8.08M, 8.25M, 8.52M, 8.92S, 9.85S (microns).

NMR ( $CCl_4$ ) Doublet centered at 3.92 $\delta$ ,  ${}^3J_{AB} = 2.5 \text{ Hz. (total area 1 proton)}$ , broad singlet 3.30 $\delta$  (area 1 proton), triplet centered at 2.38 $\delta$ ,  ${}^3J_{AB} = 6.5 \text{ Hz. (total area 2 protons)}$ , multiplet at 1.25 $\delta$ -2.2 $\delta$ , (total area 3 protons), doublet centered at 1.12,  ${}^3J_{AB} = 6.5 \text{ Hz. (total area 3 protons)}$ , triplet centered at 0.92 $\delta$ ,  ${}^3J_{AB} = 6.5 \text{ Hz. (total area 3 protons)}$  and a doublet centered at 0.67 $\delta$ ,  ${}^3J_{AB} = 6.5 \text{ Hz. (total area 3 protons)}$ .

Mass Spec Mol. wt. 144; found  $M^+ = 144$ .

Di-neopentyl acyloin

Di-neopentyl acyloin was synthesized using the same procedure as in the synthesis of dicyclohexyl acyloin. A 6.0 g. (0.042 moles) sample of freshly distilled ethyl 3,3-dimethylbutyrate (b.p. 144°, lit. 138), 144.0-144.5° at 739 mm.) was added to 23 g. of sodium to yield 1.4 g. (33.2%) of crude acyloin. The yellow oil solidified below room temperature but could not be recrystallized. Di-neopentyl acyloin was purified by GPC and collected as colorless oil.

Analysis Calc. for  $C_{12}H_{24}O_2$ : C, 71.99; H, 12.08

Found: C, 71.92; H, 12.36.

Infrared ( $CCl_4$ ) 2.87MW, 3.45S, 5.85S, 6.35-6.55S, 6.77S, 7.20M, 7.30S, 7.45M, 8.00-8.20S, 8.50MW, 9.00M, 9.35S, 10.00S (microns).

NMR ( $CCl_4$ ) Doublet of doublets centered at 4.02 $\delta$ ,  $^3J_{AB} = 9.1$  Hz,  $^3J_{AB'} = 2.7$  Hz. (total area 1 proton), broad hydroxyl singlet at 3.10 $\delta$  (area 1 proton), singlet at 2.30 $\delta$  (area 2 protons), doublet of doublets centered at 1.39 $\delta$ ,  $^3J_{AB} = 9.1$  Hz,  $^3J_{AB'} = 2.7$  Hz. (total area 2 protons), singlet at 1.02 $\delta$  (area 18 protons).

Mass Spec Mol. wt. 200; found  $M^+ = 200$ .

Synthesis of  $^{13}\text{C}$  CompoundsDiisopropyl acyloin-2- $^{13}\text{C}$ 

A 50 ml. three necked flask equipped with a syringe adapter, a nitrogen inlet, and an efficient dry-ice condenser was used to prepare isopropylmagnesium chloride. All glassware was oven dried at  $100^\circ$ . Stirring was accomplished by use of a magnetic stirrer and a powerful magnetic stirring bar. After addition of 1.75 G. of magnesium turning and 25 ml. of anhydrous ether, nitrogen was passed through the system. A solution of 2.2 ml. (2 g., 0.0254 moles) of 2-chloropropane in 5 ml. of ether was added via syringe in increments over 20 minutes. This was followed by a solution of 1.1 ml. (1 g., 0.0127 moles) of 2-chloropropane-2- $^{13}\text{C}$  (Volk Radiochemical Company, 51.5%  $^{13}\text{C}^*$ ) in 5 ml. of ether added over 10 minutes. When addition was complete the reaction was heated under gentle reflux for an additional two hours. The mixture was cooled in an ice-methanol bath, and 1.6 g. (0.16 moles) of isobutyraldehyde cyanohydrin were added slowly. The reaction was then worked up as previously described for the synthesis of isobutyroin (method 2) to yield 0.60 g. (31%) of product purified by GPC.

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\*The 2-chloropropane-2- $^{13}\text{C}$  was analyzed by mass spectroscopy and NMR. The results indicate actual  $\text{C}^{13}$  incorporation to be 40-41%.

Diisopropyl acyloin-3-<sup>13</sup>C

A Grignard carbonation apparatus similar to that described by Lemmon (139,140) was attached to a high vacuum line equipped with a manometer. All connections and stop-cocks were lubricated with high vacuum grease and tested for leaks. A 100 ml. round bottom flask was charged with 9.91 g. of barium carbonate-<sup>13</sup>C (Merck, Sharp and Dohme of Canada, Ltd., "one gram contained <sup>13</sup>C"). A pressure-equalizing dropping funnel above it was charged with 50 ml. of concentrated sulfuric acid. The entire apparatus was evacuated to 0.07 mm. for two hours. The system was vented with nitrogen and then re-evacuated to 0.07 mm. A 2 molar solution of isopropylmagnesium chloride had been previously prepared and was used as a colorless filtered solution. The 100 ml. round bottom reaction flask was isolated from the system and charged with 50 ml. of the 2 molar isopropylmagnesium chloride solution. The flask was cooled with liquid nitrogen until the ether froze and then pumped with the apparatus to 0.07 mm. (141). The whole system was isolated from the vacuum line and the Grignard solution allowed to warm up to -20°. The sulfuric acid was dropped slowly onto the barium carbonate until the pressure in the system approached 50 cm. The Grignard solution was then stirred and kept at -20° with a Dry Ice-acetone bath during carbonation. Small amounts of sulfuric acid were dropped onto the

barium carbonate in such a manner as to maintain an internal pressure of 50 to 60 cm. The solution was stirred an additional hour after uptake of carbon dioxide lessened. The flask was frozen with liquid nitrogen to absorb carbon dioxide in the system and then let warm to room temperature. The final pressure of the system was 6 cm. at  $-20^{\circ}$ . The reaction was quenched with the addition of 40 ml. of distilled water and 20 ml. of 20% sodium hydroxide (142). The mixture was poured into a 250 ml. flask containing 4 g. silver sulfate, and was heated until all the ether and some water had distilled. The grey pasty mixture was washed into a liquid-liquid extractor containing 20 ml. of 48% sulfuric acid and 50 g. crushed ice. The solution was extracted for 40 hours with ether. The ether solution was concentrated to 100 ml. and extracted with twelve 50 ml. portions of boiled distilled water. The combined water fractions were titrated with 0.50N sodium hydroxide, using a Leeds and Northrup Model 7403 pH meter, until neutral. A total of 88.20 ml. was required. The neutralized solution was washed with ether and was distilled to dryness on a rotary evaporator. A total yield of 4.73 g. (85.5%) of sodium isobutylate- $1-^{13}\text{C}$  was obtained. The 4.73 g. of sodium isobutylate- $1-^{13}\text{C}$  was added to 18 g. of triethylphosphate (143-145). A Vigreux column was added, and the mixture was heated to  $180^{\circ}$  for four hours. A total of 3.45 g. (70%) of ethyl isobutylate- $1-^{13}\text{C}$  was collected. The ester obtained was shown by NMR to contain

52%  $^{13}\text{C}$  at the 1 position. The ester was diluted 3:1 with  $^{12}\text{C}$  ethyl isobutylate and carefully distilled. The fraction distilling at 110-111° was used to synthesize isobutyroin-3- $^{13}\text{C}$  as previously described for  $^{12}\text{C}$  isobutyroin (method 1). A total of 1.60 g. (85.2%) of isobutyroin-3- $^{13}\text{C}$  was obtained.

Pivaloin-3- $^{13}\text{C}$  (di-t-butyl acyloin-3- $^{13}\text{C}$ )

The apparatus and procedures used in the synthesis of isobutyroin-3- $^{13}\text{C}$  were used to synthesize pivaloin-3- $^{13}\text{C}$ . A 5.00 g. sample of barium carbonate (Merck, Sharp, and Dohme of Canada, Ltd., "one gram contained  $^{13}\text{C}$ ") and 80 ml. of a 1.0 molar *t*-butyl magnesium chloride solution were reacted to yield 2.96 g. (89.2%) of sodium pivalate. The dried salt was added to 18 g. of freshly distilled triethyl phosphate and heated to 180° under a Vigreux column. After four hours, 0.945 g. (30.8%) of ethyl pivalate-1- $^{13}\text{C}$  was collected. The ester was shown by NMR to contain 50%  $^{13}\text{C}$  at the carbonyl carbon. The ester was diluted 3:1 with ethyl pivalate and redistilled. The fraction distilling at 116-118° was collected. A 1.50 g. (0.011 moles) sample of the above ester was added to 0.6 g. of sodium sand in 30 ml. of ether and treated as in the synthesis of dicyclopropyl acyloin. Total yield of pivaloin-3- $^{13}\text{C}$  was 0.45 g. (47.8%).

Di-t-butyl ketone-3- $^{13}\text{C}$

The procedure of Petrov (146,147) for *t*-butyl lithium addition to esters was adapted to small scale reactions. The apparatus used was previously described for the synthesis of

isobutyroin-2- $^{13}\text{C}$ . The flask was charged with 7 ml. of 1.85 molar solution of t-butyl lithium in n-pentane and cooled to  $-40^\circ$  with a Dry Ice-acetone bath. A total of 1.28 g. of ethyl pivalate-1- $^{13}\text{C}$  (16%  $^{13}\text{C}$ ) was added dropwise via a syringe. The solution was kept at  $-40^\circ$  throughout the addition and was then allowed to reach room temperature. Stirring was maintained for an additional three hours. The reaction mixture was cooled and quenched with the addition of 2 ml. of water followed by drops of hydrochloric acid. The ether layer was collected and washed with saturated sodium bicarbonate solution. The water layer and bicarbonate wash were extracted with 5 ml. portions of ether. The combined ether layer was dried over anhydrous sodium sulfate and reduced by careful distillation to 2 ml. Di-t-butyl ketone-3- $^{13}\text{C}$  (148) was isolated in 20% yield by GPC as a colorless liquid.

## APPENDICES

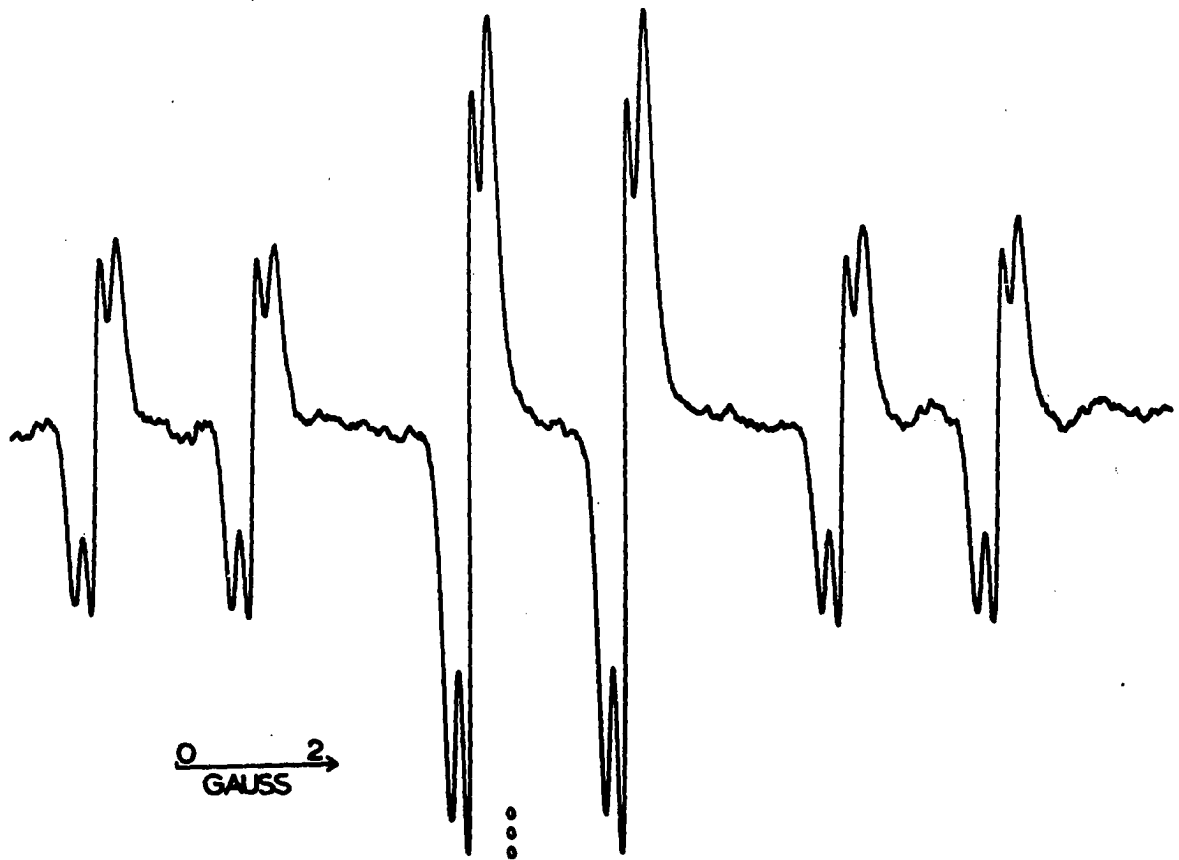
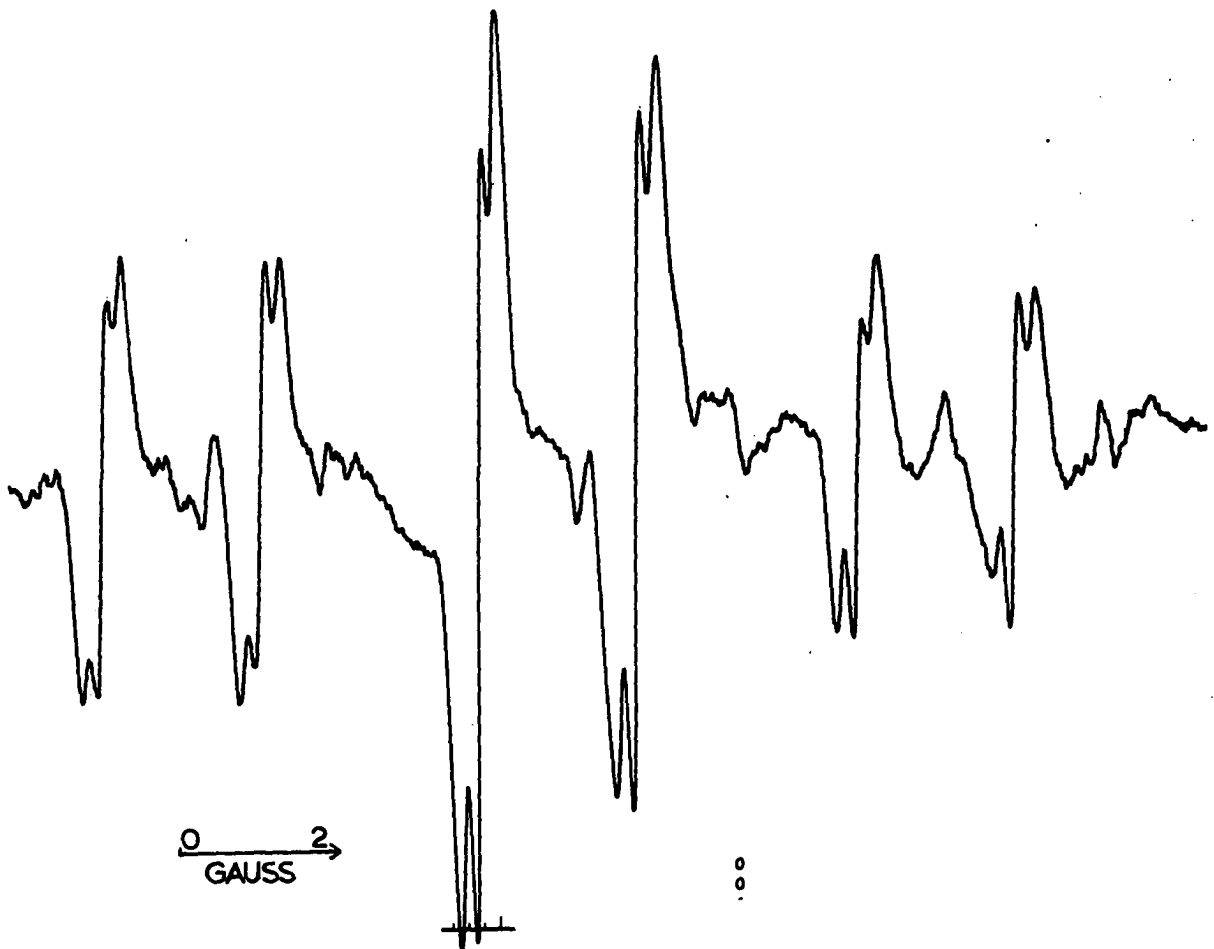
 $\alpha,\beta$ -Unsaturated Semidiones

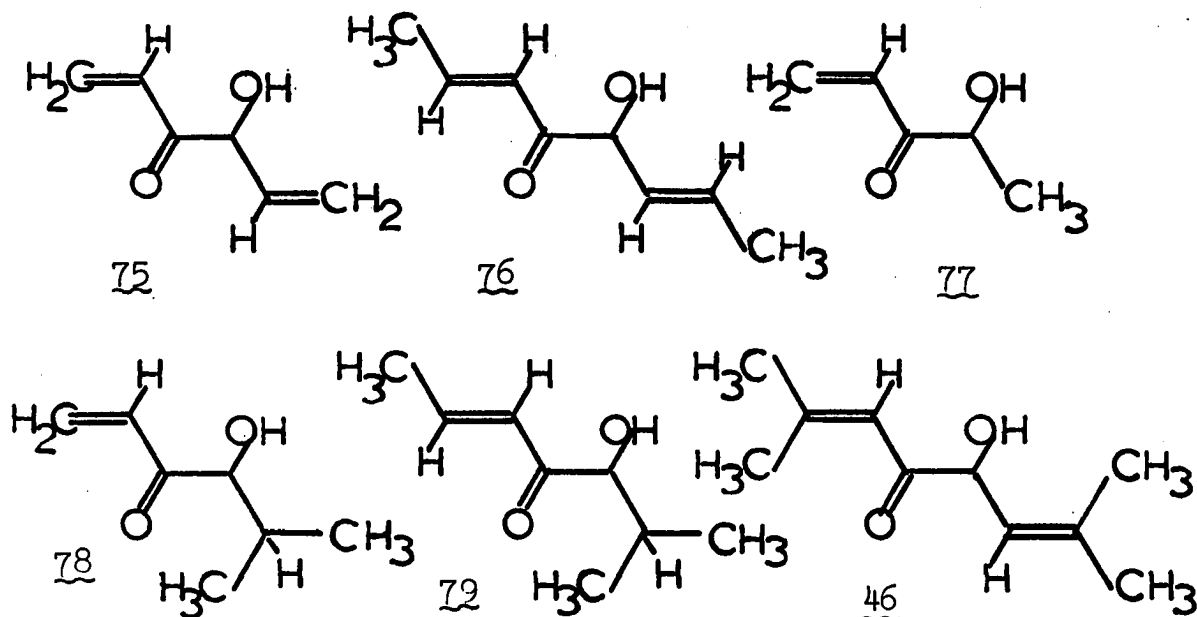
An attempt was made to prepare semidiones containing an  $\alpha,\beta$ -double bond. Acyloin condensations failed to yield either 4-hydroxy-1,5-hexadien-3-one (compound 75) or 5-hydroxy-2,6-octadien-4-one (compound 76). 4-Hydroxy-1-pent-3-one (compound 77) and 5-methyl-4-hydroxy-1-hexen-3-one (compound 78) were prepared from cyanohydrin addition to vinylmagnesium chloride. The hydroxyketones were isolated as main components of mixtures of isomers. The ESR signals generated from these mixtures were inconsistent with the structure. 2-Methyl-4-hydroxy-5-hepten-3-one (compound 79) was synthesized by the addition of crotonaldehyde cyanohydrin to isopropylmagnesium chloride. The hydroxyketone was purified by GPC and gave consistent NMR, IR and elemental analyses. The synthesis of this compound is reported in the experimental section, page 148. When compound 79 was added to molar quantities of potassium *t*-butoxide in deoxygenated DMSO, a complex mixture of radicals was formed. In an excess of base, compound 79 formed a radical which displayed the spectrum shown in Figure 30a. This spectrum is identical with that of isopropyl propyl semidione (Figure 30b) and consists of a large triplet splitting of 4.57 g., a doublet splitting of 1.95 gauss, and a small triplet splitting of 0.22 gauss. A



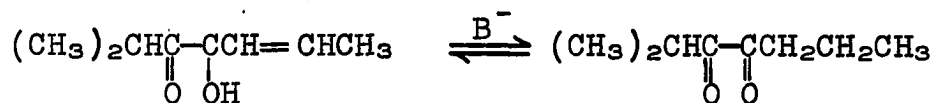
Figure 30. (a) First-derivative ESR spectrum of 2-methyl-4-hydroxy-5-hepten-3-one (top) in DMSO and excess base.

(b) First-derivative ESR spectrum of isopropyl propyl acyloin (bottom) in DMSO.





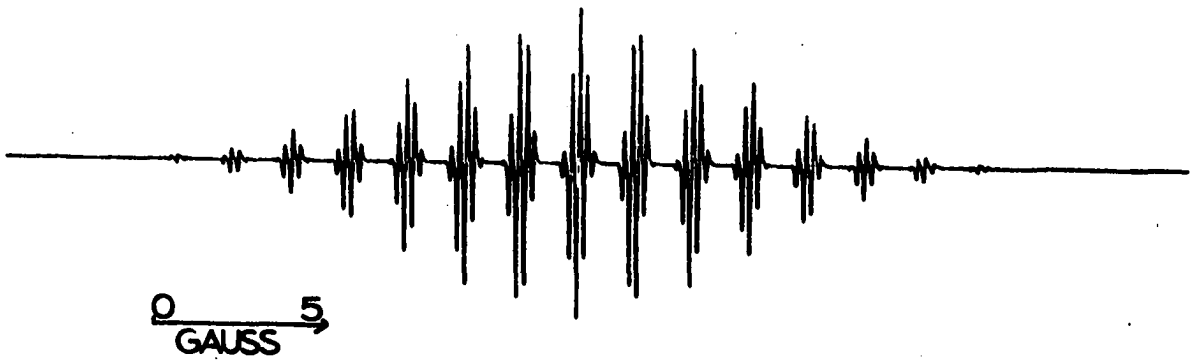
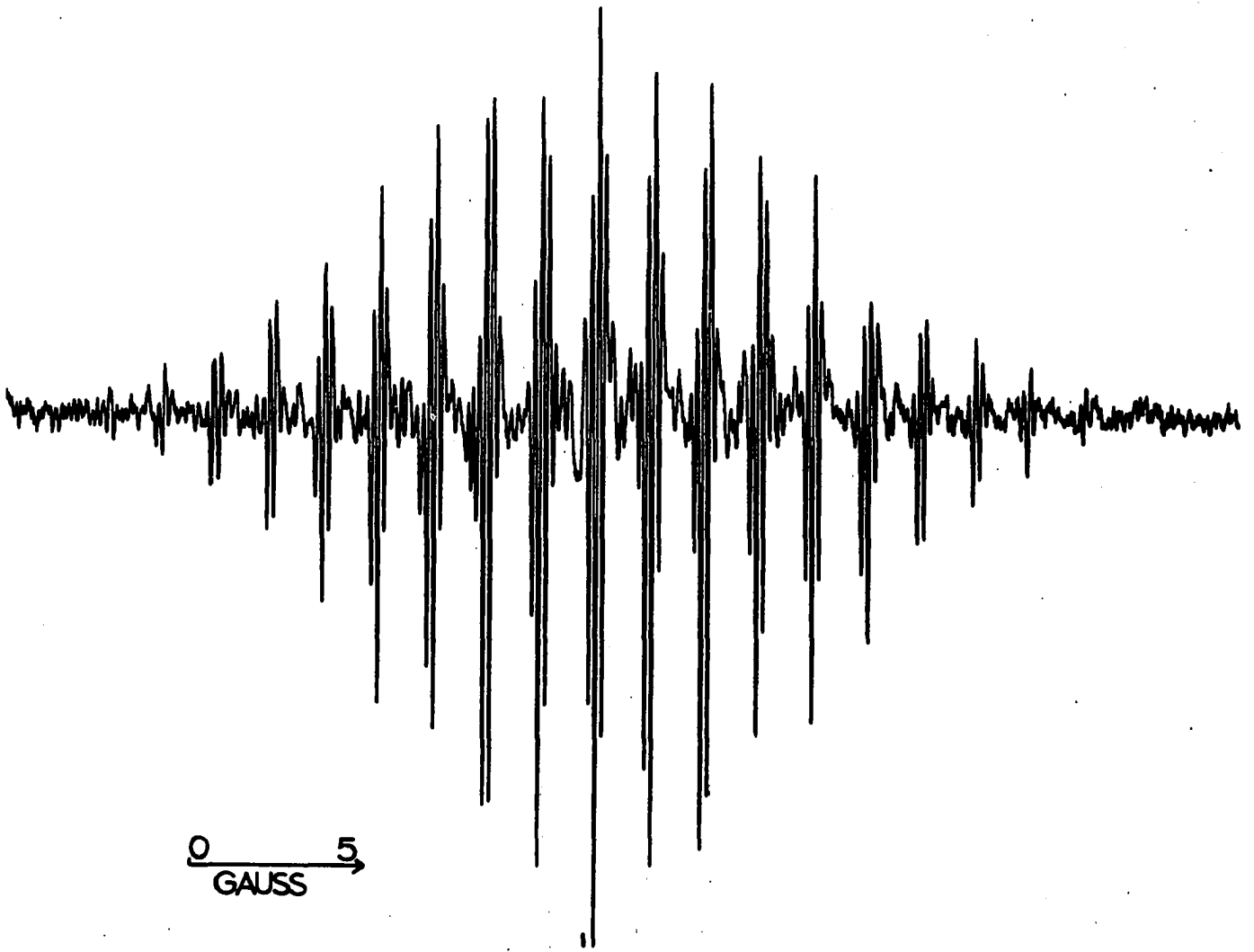
possible mechanism for this reaction involves base catalyzed tautomerization of 79 to isopropyl propyldione.



The dione then can be reduced by hydroxyketone to form isopropyl propyl semidione.

An attempt was made to synthesize 2,7-dimethyl-5-hydroxy-2,6-octadien-4-one (compound 46). The acyloin condensation of ethyl 3,3-dimethylacrylate in sodium sand and ether resulted in a complex mixture. The mixture was fractionated by GPC. One fraction collected, when heated with potassium t-butoxide and DMSO, gave the spectrum shown in Figure 31. The GPC fraction gave the following analyses:

Figure 31. First-derivative ESR spectrum of 2,7-dimethyl-2,6-octadien-4,5-dione (top) in DMSO; calculated spectrum (bottom) for Lorentzian linewidth of 0.075 gauss and splitting constants from text performed by JEOLCO JNM-RA-1 spectrum accumulator.



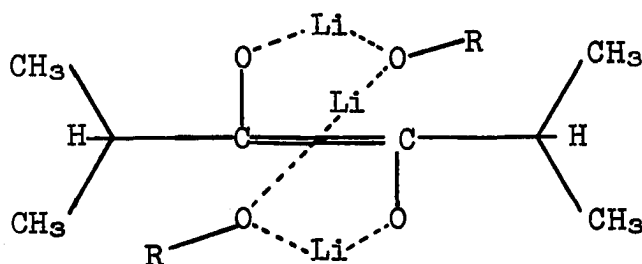
Infrared: (CCl<sub>4</sub>) 3.48S, 5.80-6.10VS, 6.20M, 6.35W, 6.95S, 7.10M, 7.25S, 7.32S, 7.73M, 8.05S, 8.54S, 8.73S, 8.80S, 8.95M, 9.25W, 9.43M (microns).

NMR: (CCl<sub>4</sub>) A singlet at 1.90 $\delta$  (area 6 protons), singlet at 2.10 $\delta$  (area 6 protons), a multiplet at 5.65-6.00 $\delta$  (total area 2 protons, a singlet at 1.00 $\delta$  (area 9 protons, and a singlet at 1.07 $\delta$  (area 6 protons).

The mass spectrum indicated a high molecular weight component. The NMR and IR suggested a mixture of diketone and other material. Elemental analyses (Calc. for C<sub>10</sub>H<sub>16</sub>O<sub>2</sub>: 71.30% C, 9.60% H. Found: 64.04% C, 8.61% H [Schwartzkopf Microanalytical Laboratory, Woodside, N. Y.]. Found: 66.05% C, 8.81% H [Galbraith Laboratories, Inc., Knoxville, Tenn.]) gave a low percentage of carbon indicating possible air oxidation of the diene. The spectrum of the radical shown in Figure 31 can be explain in terms of a 3.12 gauss heptet, a 1.56 gauss heptet, and a 0.21 gauss triplet. The small triplet can be assigned to the  $\alpha$  hydrogen atoms. However, more information is required before assigning the two methyl splittings.

## Lithium Complex of Diisopropyl Semidione

When diisopropyl semidione is generated in DMSO in the presence of lithium iodide, the spectrum shown in Figure 32 is obtained. The spectrum can be explained in terms of one large lithium splitting of 0.65 gauss, two small lithium splittings of 0.15 gauss, and two hydrogen splittings of 2.08 gauss. This explanation requires a bridged radical species. The bridged trans semidione structure shown in diagram 80 is one possibility.

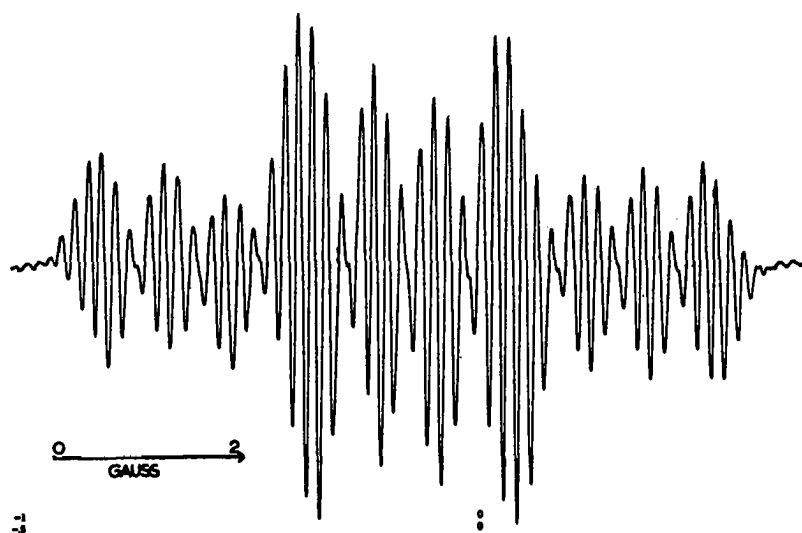
80

However, the spectrum may also be explained in terms of a cis structure with 12  $\beta$  hydrogen atom splittings of 0.15 gauss, two  $\alpha$  hydrogen atom splittings of 2.08 gauss, and one lithium atom splitting of 0.65 gauss. The center seven lines of a thirteen line binomial pattern would be approximately in the ratio of 2:5:8:9:8:5:2 as compared with 1:2:3:4:3:2:1 for two lithium atoms.

The latter explanation is more consistent with the results found in the dimethyl semidione system. The dimethyl

Figure 32. First-derivative ESR spectrum of diisopropyl semidione in DMSO containing lithium iodide.





semidione radical anion in the presence of lithium iodide was studied by Mr. Dave Lawson. The spectrum of this radical demanded six hydrogen atom hfsc of 7.5 gauss and one lithium atom hfsc of 0.60 gauss. The magnitude of the methyl splittings suggests the expected cis isomer. The lithium splitting constant is similar to the one found in diisopropyl semidione.

It may be that cis diisopropyl semidione has an  $\alpha$  hydrogen atom hfsc equal or nearly equal to that of the trans isomer. In DMSO only a 2.02 gauss splitting constant is observed and this is assumed to be 100% trans. However, Norman and Pritchett (149) have observed cis diisopropyl semidione in aqueous methanol. They assigned a 2.45 gauss to the  $\alpha$  methine hydrogen atoms in the cis isomer and 1.7 gauss to the trans isomer. Heller (150) reported only one isomer of 2.00 gauss hfsc in alcohol-water mixtures.

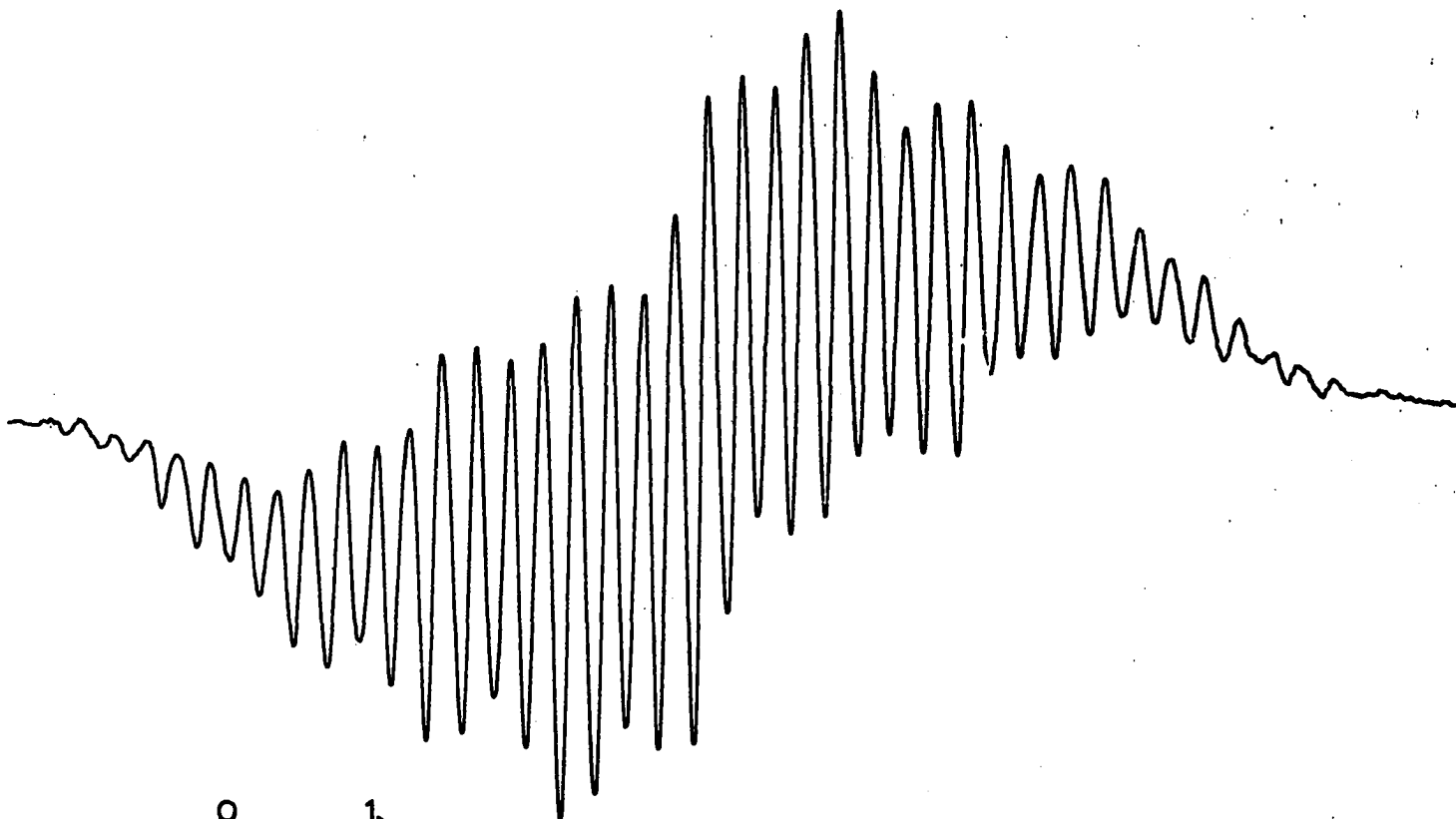
### In situ Benzoin Condensations

The generation of semidione radical anions was attempted from in situ benzoin condensations. A total of 20 microliters of aldehyde was added to 0.1 ml of 1N potassium cyanide in one side of an ESR H cell. One drop of ethanol was added to dissolve the products. A two molar excess of potassium t-butoxide and one milliliter of DMSO was added to the other half of the cell. The solutions were purged with nitrogen for 25 minutes and then mixed as usual to produce a radical.

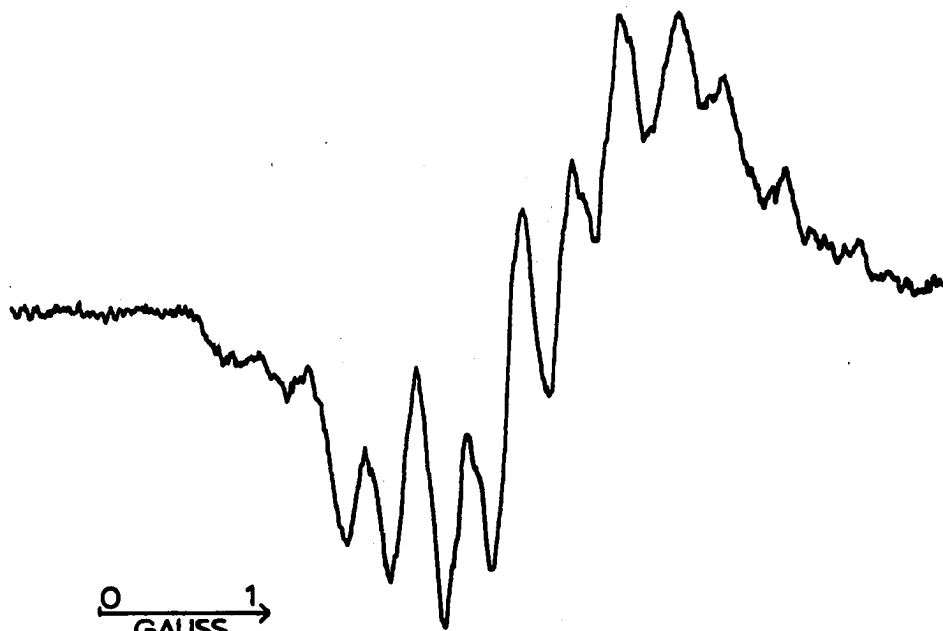
Benzaldehyde, furfural, and thiophenal yielded the corresponding semidiones. Cyclopropylcarboxaldehyde, cyclooctanecarboxaldehyde, acetaldehyde, pivaldehyde, acrolein, and crotonaldehyde failed to give an ESR signal. Acrolein cyanohydrin and crotonaldehyde cyanohydrin, when treated with base and DMSO in the absence of oxygen, also failed to give a signal.

2-Naphthaldehyde and 1-naphthaldehyde yielded the ESR spectra shown in Figure 33. Due to the large number of triplet splittings expected, no assignments have been made. It is interesting to note that the weak signal found for the semidione of 1,1'-naphthoin can be explained in terms of two  $\beta$ -atom interactions as opposed to one such interaction in the semidione of 2,2'-naphthoin (diagram 81).

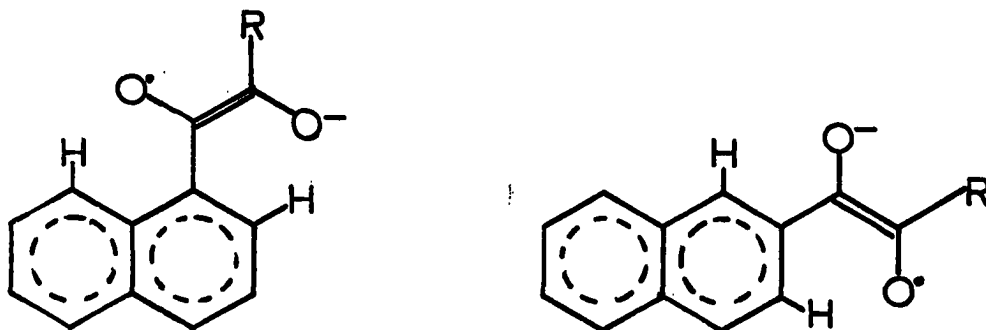
Figure 33. (a) First-derivative ESR spectrum of a radical generated in DMSO from the benzoin condensation product of 2-naphthaldehyde (top).  
(b) First-derivative ESR spectrum of a radical generated in DMSO from the benzoin condensation product of 1-naphthaldehyde (bottom).



0 1  
GAUSS

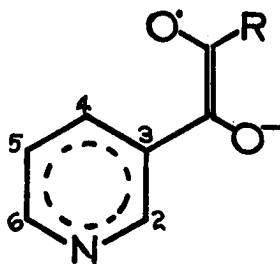


0 1  
GAUSS



81

2-Pyridinecarboxaldehyde gave the weak spectrum shown in Figure 34a. The spectrum, probably is a 1:2:3:2:1 pentet of 0.86 gauss hfsc for two nitrogens. 4-Pyridinecarboxaldehyde gave the ESR spectrum shown in Figure 34b. The spectrum can be analyzed for two nitrogen splittings of 2.6 gauss. The fine structure could be a 0.5 gauss 1-4:6:4:1 pentet for four ortho hydrogen atoms. 3-Pyridinecarboxaldehyde yielded the strongest signal of the series (Figure 35). The spectrum was simulated using the following splitting constants: 0.140 (2N), 2.00 (2H), 0.80 (2H), 0.27 (2H), 0.14 (2H).



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- Figure 34. (a) First-derivative ESR spectrum of a radical generated in DMSO from the benzoin condensation product of 2-pyridine-carboxaldehyde (top).
- (b) First-derivative ESR spectrum of a radical generated in DMSO from the benzoin condensation product of 4-pyridine-carboxaldehyde (bottom).

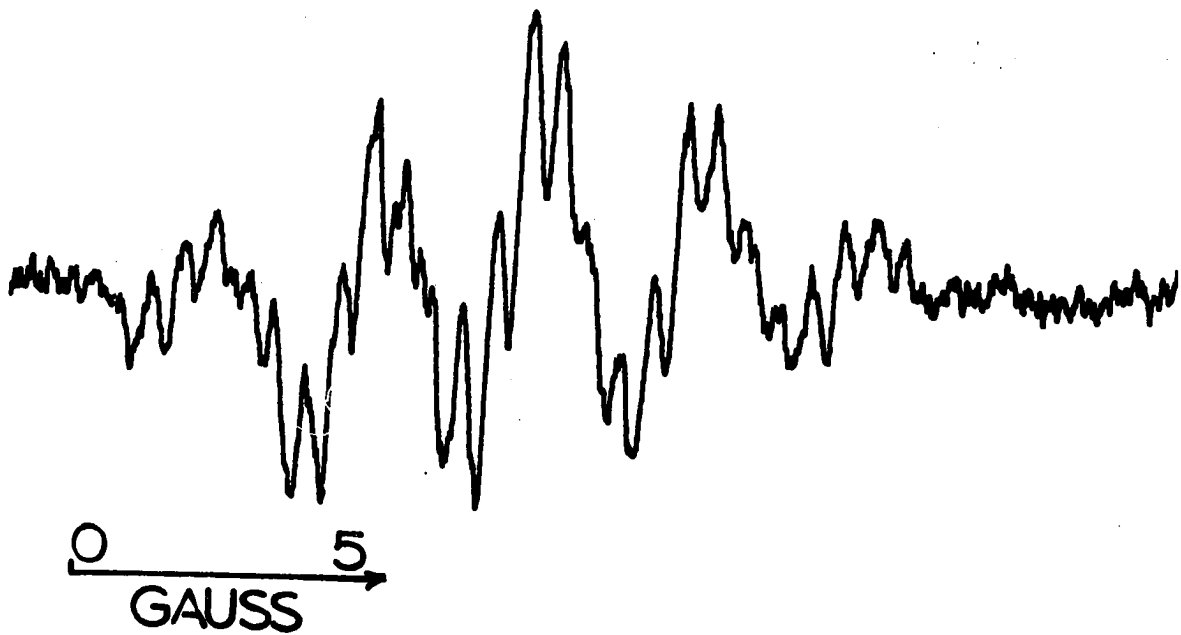
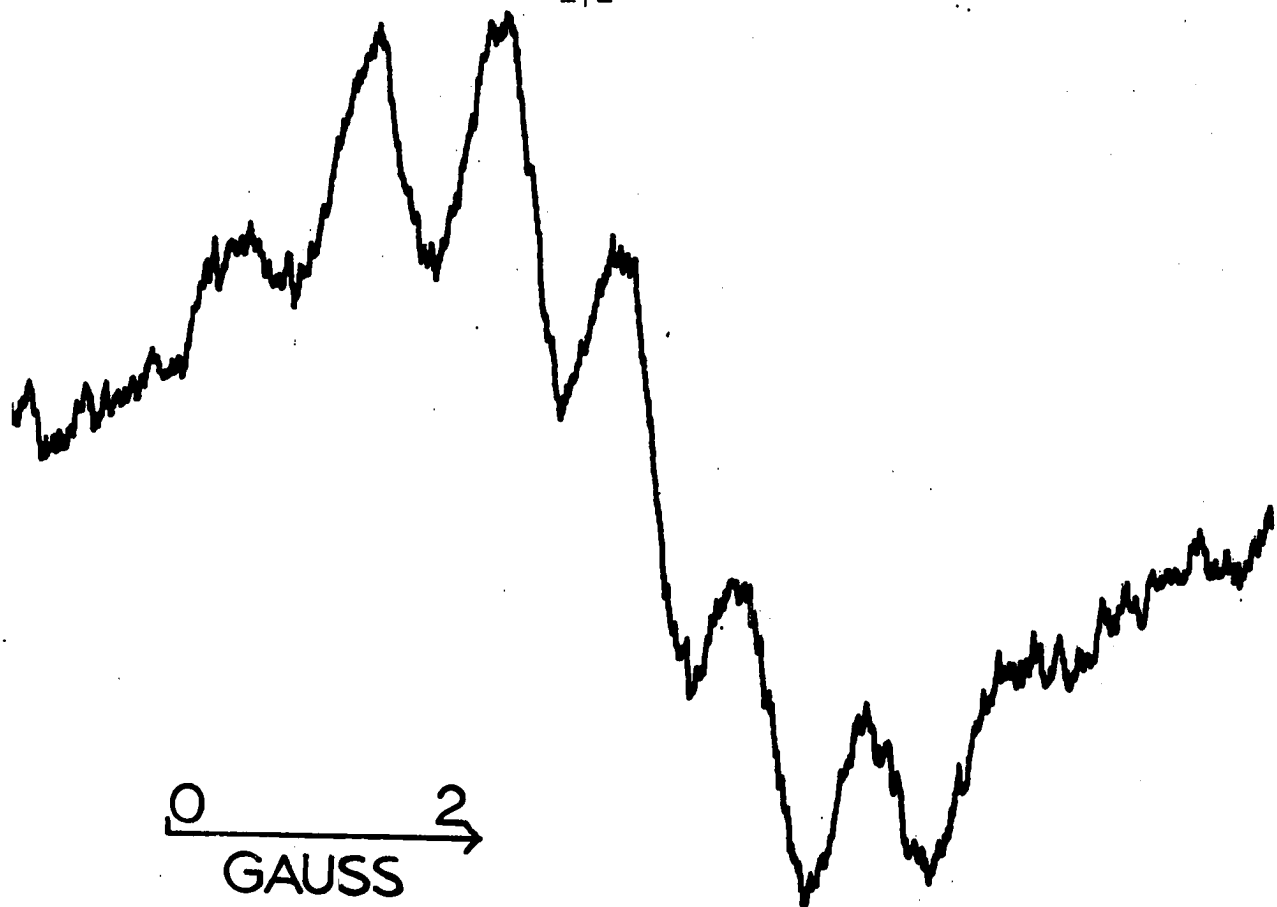
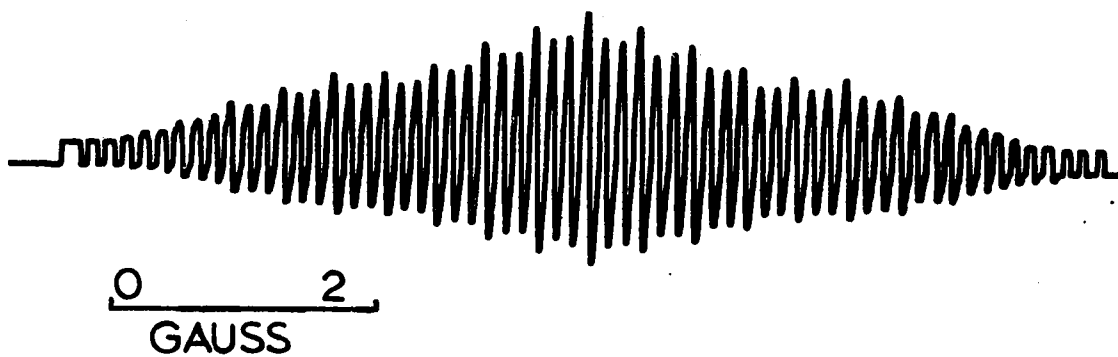
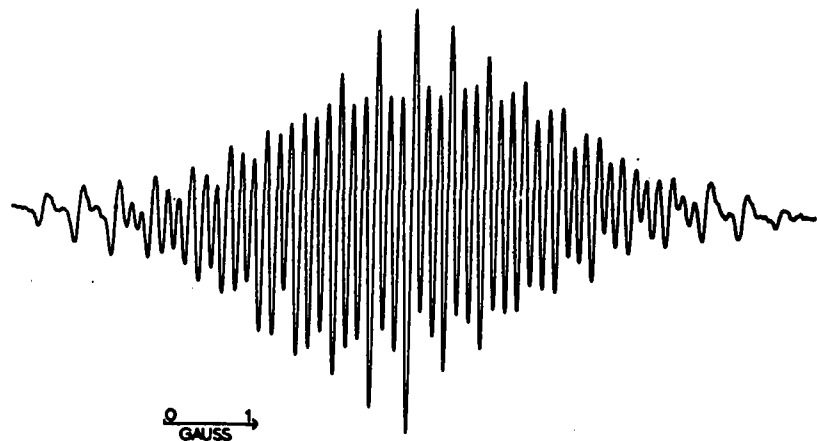




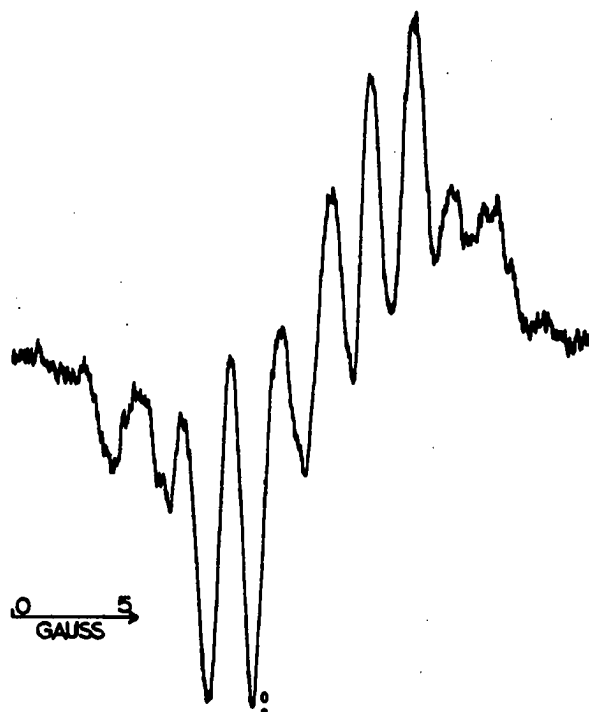
Figure 35. First-derivative ESR spectrum of a radical generated in DMSO from the benzoin condensation product of 3-pyridinecarboxaldehyde (top); calculated spectrum (bottom) for Lorentzian linewidth of 0.075 gauss and splitting constants from text performed by JEOLCO JNM-RA-1 spectrum accumulator.



The large triplet is probably due to hydrogen atoms  $H_a$  in diagram 82. The small triplet may be due to the  $H_b$ . The remaining triplet splittings might be assigned to either of the two remaining hydrogen atoms.

Cinnamaldehyde gave a weak ESR spectrum shown in Figure 36. The spectrum consists of 7 or 9 lines separated by 2.3 gauss. No assignments could be made.

Figure 36. First-derivative ESR spectrum of a radical generated in DMSO from the benzoin condensation product of cinnamaldehyde.



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