1969

Semidiones derived from bicyclic hydrocarbons

Philip Rodger Whittle
Iowa State University

69-20,685

WHITTLE, Philip Rodger, 1943-

SEMIDIONES DERIVED FROM BICYCLIC HYDROCARBONS.

Iowa State University, Ph.D., 1969
Chemistry, organic

University Microfilms, Inc., Ann Arbor, Michigan

SEMIDIONES DERIVED FROM BICYCLIC HYDROCARBONS

by

Philip Rodger Whittle

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

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

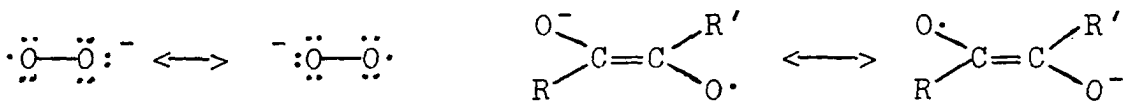
1969

TABLE OF CONTENTS

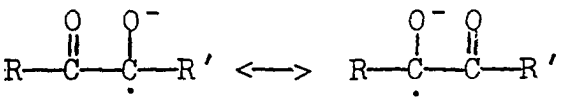
INTRODUCTION

Brief Survey of Semidiones

Semidiones can be considered to be vinylogs of the resonance stabilized superoxide ion (a) with resonance contributions shown in b, or as α-keto ketyls (c). Semidiones



a b



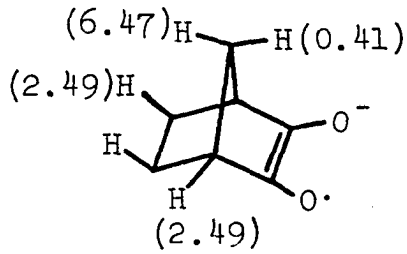
c

with aryl R groups were studied in 1963 (1) while the first aliphatic semidiones were observed by Russell and Strom in 1964 (2).

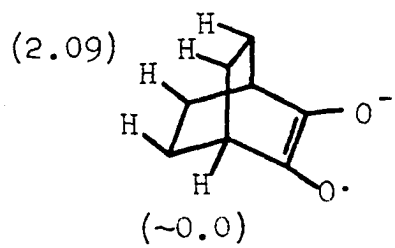
Since these initial experiments, a large volume of work has been carried out in these laboratories employing the semidione spin label in rather complicated organic molecules. Electron spin resonance (ESR) studies of semidiones derived from steroids and decalones have proven very helpful in assigning the configuration at distant centers in the molecule (3-6). A detailed study of substituted cyclohexanesemidiones has furnished interesting thermodynamic data for ring inversion in substituted cyclohexenes (7). These and

other applications of the ESR study of semidiones have been reviewed (8-10).

One of the most powerful uses of the semidione spin label involves rigid polycyclic compounds. This becomes especially evident when one considers the semidiones in the bicyclo-[2.2.1]heptane (d) and bicyclo[2.2.2]octane (e) systems (11, 12). First, note the absence (or extremely small)



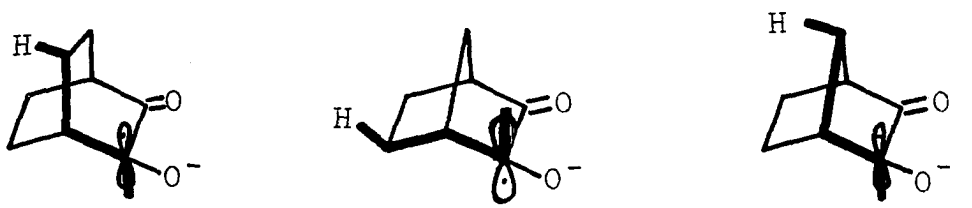
d



e

interaction of the bridgehead hydrogens in e, whereas the bridgehead hydrogens in d have appreciable spin density. This was explained (9) on the basis of the Heller-McConnell equation (13), $a^H = \beta\rho_C Cos^2\theta$, where β is a constant, ρ_C is the spin density at carbon and θ is the dihedral angle between the C-H bond involved and the p_z orbital in the π-system. In e, $\theta = 90°$, and one predicts no interaction by this directed mechanism (hyperconjugation), whereas in d, $\theta < 90°$, and this hydrogen does interact with the unpaired spin. Secondly, note that all the β-hydrogens which interact in these systems, with the exception of the syn-7-hydrogen in

d, are part of a "W" or "2V" arrangement (i.e., the H-C-C-C bonds and one-half of the p_z orbital containing the unpaired spin define a W) as illustrated in f by the bold lines. This relationship of bonds is very important in both NMR



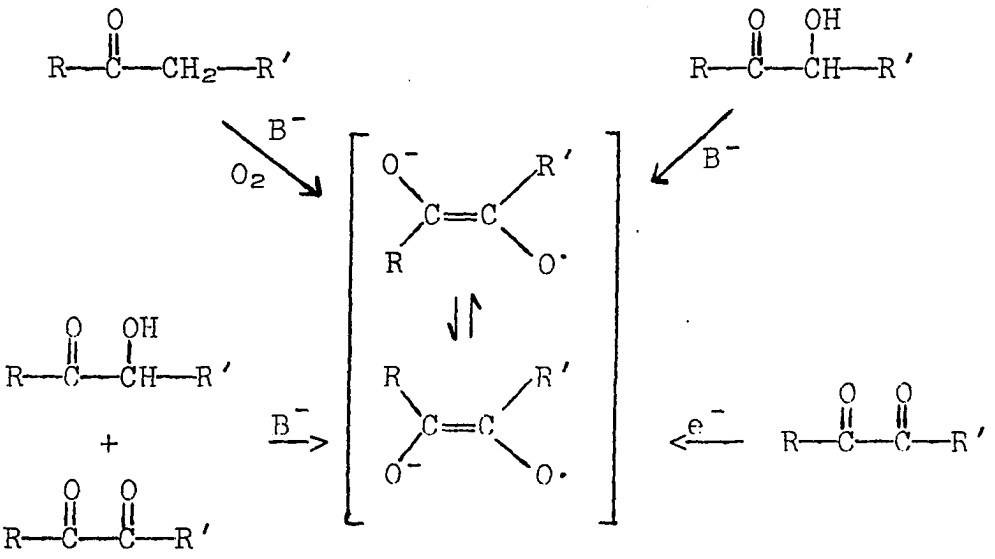
f

(14, 15) and ESR (11, 12) couplings and will be utilized many times in this thesis to assign hyperfine splittings.

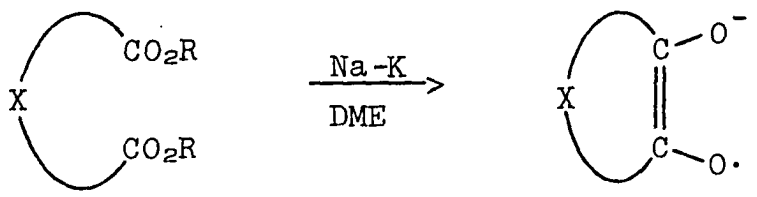
From these two examples of bicyclic semidiones, one might conclude that given a general understanding of the patterns of interactions of specific hydrogens in a variety of bicyclic systems, this technique could provide a powerful tool in the structure determination of bicyclic compounds. One of the primary goals of this thesis is to provide a part of this general understanding. Specifically, we want to examine the effects of small changes in geometry upon the long range interactions in semidiones.

With the above ideas in mind, the major problem is that of introducing the semidione spin label in the desired system. In general, semidiones have been prepared by the methods in Chart I. In certain bicyclic systems, such as

Chart I



bicyclo[2.2.2]octanes, the ketones cannot be oxidized directly with base and oxygen (12), so one must resort to a higher oxidation state such as the diketone or α-hydroxy ketone. These are difficult to obtain in many cases, especially when the molecule contains other sensitive functional groups. We introduce here the acyloin condensation as a very versatile method of generating a vast array of bicyclic semidiones from the appropriate dicarboxylic esters as shown in g. This route has been especially useful in the preparation of strained polycyclic systems.

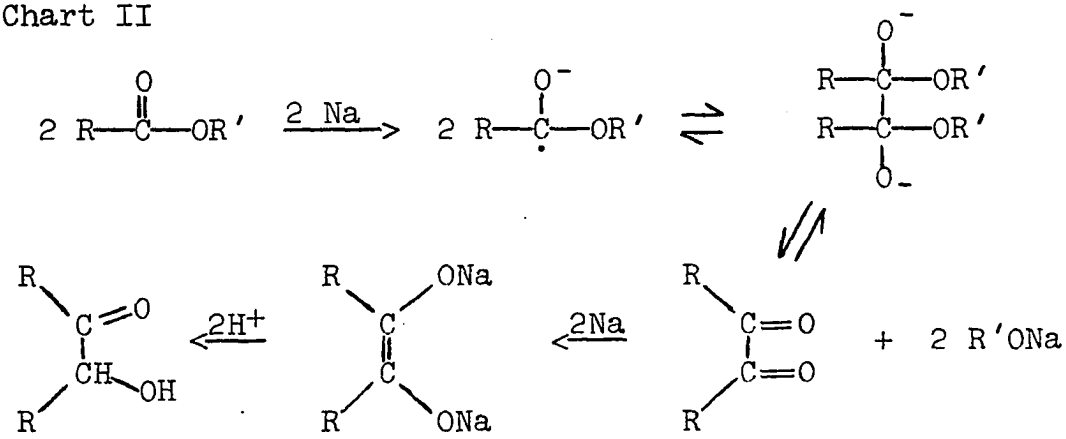


g

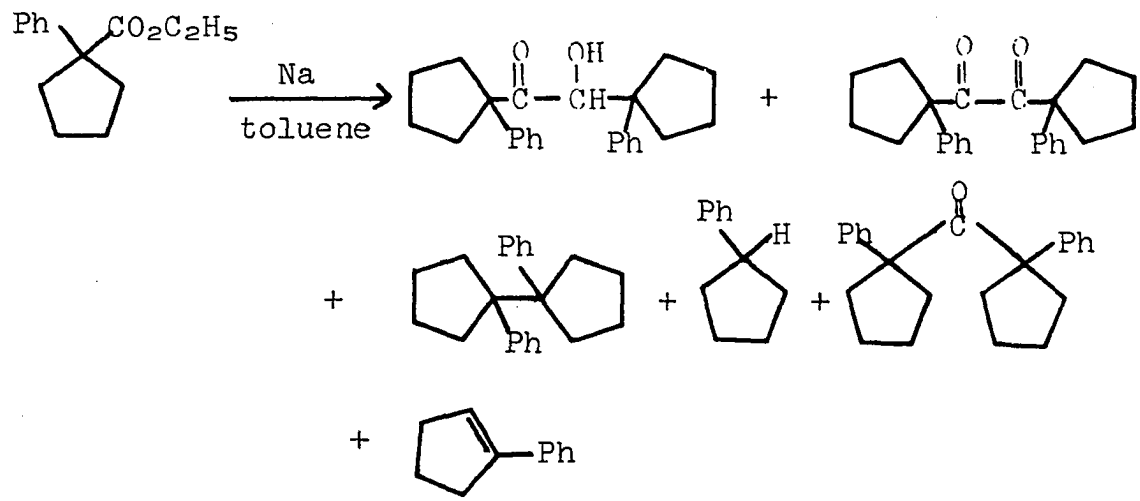
The Acyloin Condensation

The acyloin condensation was discovered in 1903 by Bouveault and Blanc (16). Since this time, the reaction has been used rather extensively as a synthetic tool. Much of this synthetic work has been reviewed (17, 18). Very little work has been directed toward establishing a mechanism for the reaction. The general mechanism which is most consistent with the experimental facts is shown in Chart II.

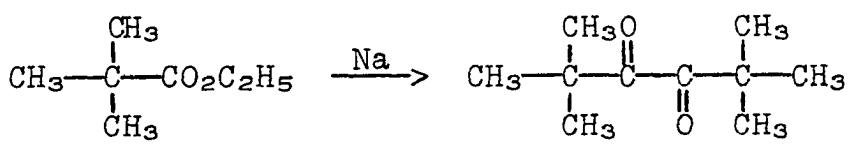
Chart II



Very convincing evidence for the free radical nature of the reaction was provided by van Heyningen (19) who observed, in addition to the expected acyloins, a number of "free radical" products from selected systems in which the intermediate carbon radicals (derived from the ketyl) have enhanced stability, for example:



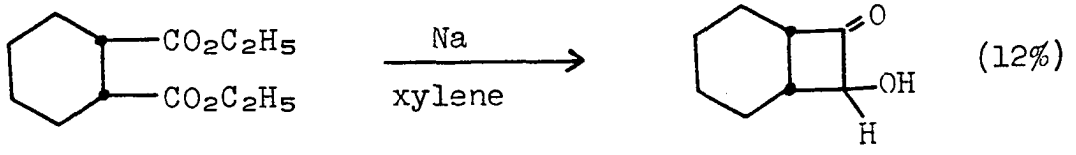
The diketone is generally believed to be a discrete intermediate in the reaction, since it is sometimes the major isolated product in those cases in which it is resistant to further reduction. This was the case in the acyloin condensation of ethyl pivalate (20):



The most important application of the acyloin condensation is to effect ring closures using the appropriate dicarboxylic esters as substrates. The size of the ring formed in the product is a major factor in the reaction. Since very little kinetic work exists (21), one must look at product yields for general trends. Poor to moderate yields (10-50%) of five-membered ring acyloins are usually

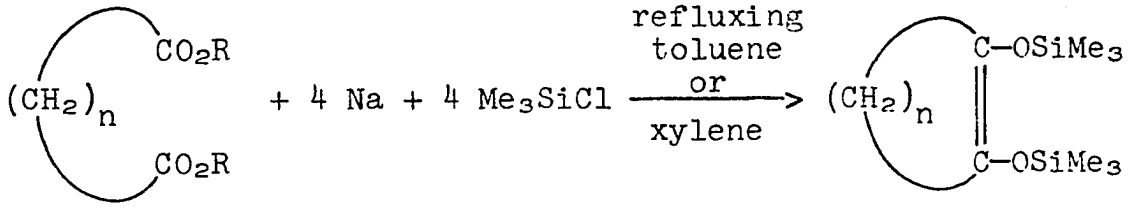
obtained whereas moderate to good yields (40-70%) of six, seven and other medium ring acyloins are usually realized. In general, very good yields of large ring acyloins are realized.

At the time of Finley's review (18) in 1964, the only report of the successful preparation of a small ring acyloin was due to Cope and Herrick (22):



(12%)

The introduction of the chlorotrimethylsilane trapping technique (h) by Schräpler and Rühlmann (23) in 1964, and

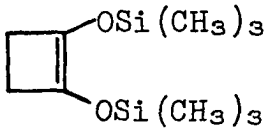


+ 4 NaCl + 2 ROSiMe3

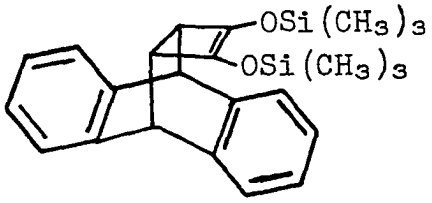
h

their discovery that the bis(trimethylsiloxy)alkenes could readily be hydrolyzed to the corresponding acyloins, opened up a new route to small ring acyloins. Rühlmann, Seefluth and Becker further demonstrated the usefulness of this

technique by synthesizing the four-membered ring derivatives i and j in high yields (24). This technique has been employed by others to obtain substituted four-membered ring acyloins



i



j

(25) and a series of bicyclo[4.2.0]octane derivatives with the acyloin moiety in the four-membered ring (26).

As Bloomfield (27) has pointed out, excess chlorotrimethylsilane acts as a scavenger for alkoxides produced in the reaction, so the solution remains essentially neutral. Hence, the acyloin products are favored, and other processes, such as Dieckmann condensations, are essentially eliminated. This becomes especially important in the attempted synthesis of small strained ring compounds.

We have used this trapping technique, in addition to the direct acyloin condensation with sodium-potassium alloy in 1,2-dimethoxyethane (DME) to produce a variety of polycyclic semidiones, many containing a four-membered ring.

RESULTS AND DISCUSSION

Semidiones *via* the Acyloin Condensation

Since the diketone is a postulated intermediate in the acyloin condensation, one might expect to be able to see the corresponding one electron reduction product (semidione) if the reaction were carried out in the cavity of an electron spin resonance (ESR) spectrometer. (Semidiones can be prepared by alkali metal reduction of α-diketones (28)). In an attempt to develop a feasible method for the generation of the semidione derived from biacetyl, with carbon-13 enrichment in a specific position, Dr. Graham Underwood[a] was able to obtain a very weak ESR spectrum when ethyl acetate was reacted with sodium-potassium alloy in an ethereal solvent such as 1,2-dimethoxyethane (DME). Although this route was not very acceptable for preparing acyclic semidiones, it suggested a new, convenient method for preparing heretofore rather inaccessable bicyclic semidiones from the appropriate diesters.

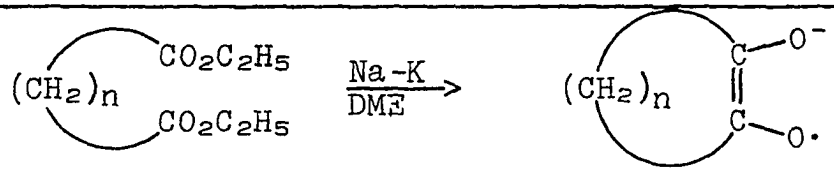
In order to explore the utility of this method, the diethyl esters of succinic, glutaric, adipic and pimelic

---

[a]Underwood, Graham, Department of Chemistry, New York University, University Heights, Bronx, N.Y. Data from postdoctoral research at Iowa State University. Private communication. 1967.

acids were reacted with an excess of sodium-potassium alloy in DME (in an ESR cell). The results in Table 1 were obtained. When longer chain diesters (n = 6, 7, 8, 10, 14) were studied, extremely low concentrations of radicals were obtained.

Table 1. Monocyclic semidiones *via* the acyloin condensation in DME



	Hyperfine Splitting Constants (gauss)		
n	Observed	Reported	Reference
2	14.4 (4H)	13.55 (4H)[a]	7
3	13.8 (4H)	13.12 (4H)[b]	6
4	10.2 (4H)	9.83 (4H)[b]	4
5	7.1 (2H)	6.63 (2H)[a]	7
	2.1 (2H)	2.00 (2H)	

[a]In N,N-dimethylformamide.

[b]In dimethyl sulfoxide.

This was not really surprising, since these larger ring semidiones are observed in very low yield by reaction of the isolated acyloin with base in DMSO (standard technique), a fact which is not fully understood.

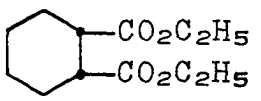
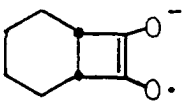
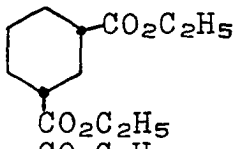
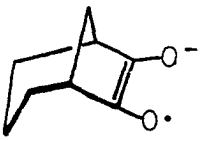
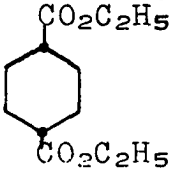
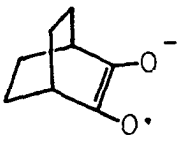
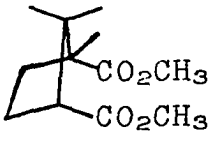
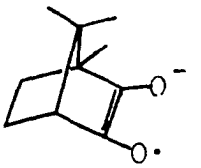
Other solvents were employed in the reaction (such as

tetrahydrofuran) but DME seemed to be the best choice of solvent. The initial sodium-potassium alloy employed consisted of one part sodium (by weight) to five parts potassium. It was later observed that better results were obtained with an alloy containing more sodium. A one-to-one ratio of the two metals provided an alloy which was suitably liquid above 10°C and proved most useful for our purposes.

In order to test the usefulness of this method for generating bicyclic semidiones, some cis-cycloalkane dicarboxylic acid esters were studied which would give semidiones which were known. These results are shown in Table 2. A large number of bicyclic semidiones have been obtained by this method and are discussed in the appropriate section of this thesis. A preliminary report of this work has been published (29).

It will be noted from Tables 1 and 2 that the hyperfine splitting constants observed in DME are in general somewhat larger than those reported in DMSO for the same radical anion. This effect is observed in all systems which we have studied and must be due to a difference in solvation of the radical anion in the two solvents. Solvent effects upon the hyperfine splitting constants in a variety of types of radicals have been discussed. The variation of splitting constants has been correlated with various solvent properties such as its dielectric constant (30), dipole moment (31), ionization

Table 2. Bicyclic semidiones *via* acyloin condensation in DMF

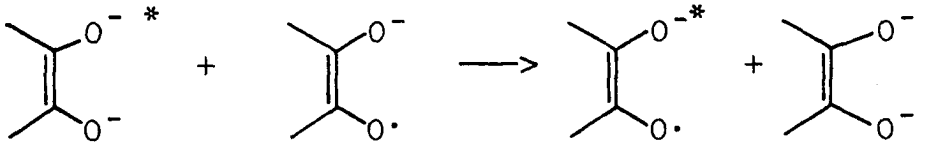
Diester	Semidione	Hyperfine Splitting Constants (gauss) Observed	Reported[a]	Ref
		13.5 (2H) 0.5 (2H) 0.25 (2H)	---	---
		5.7 (2H) 4.0 (1H) 0.6 (5H)	5.51 (2H) 4.03 (2H) 0.53 (5H)	11
		2.13 (4H)	2.09 (4H)	12
		2.8 (2H) 2.3 (1H) 0.6 (3H)	3.01 (2H) 2.08 (1H) 0.55 (3H) 0.22 (1H) 0.15 (3H)	32

[a]In DMSO.

potential (33), etc., depending upon the investigator and the type of radical studied. The solvent effects upon substituted benzosemiquinones have been studied quite extensively, and the change in hyperfine splitting constants have been related to the ion-solvating power of the solvent (34, 35). The present results are in agreement, qualitatively, with those

studies.

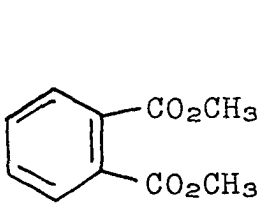
In some favorable cases, in which the acyloin condensation proceeds very well under these experimental conditions, the ESR spectra obtained are often poorly resolved and the lines are rather broad. This probably arises from rapid electron transfer between the dianion and the semidione. Since an excess of sodium-potassium alloy is used, the dianion is probably present in appreciable concentrations. A simplified picture of this exchange process is:



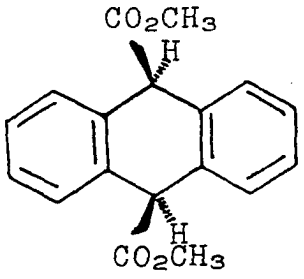
Only when the lifetime of a given radical anion is large in comparison to the reciprocal of the hyperfine coupling constant, can this splitting be well resolved. Smentowski and Stevenson (36) have shown the major source of line-broadening in the cyclooctatetraene radical anion is electron transfer from the cyclooctatetraene dianion, when concentrations greater than 0.03 M are involved.

This line broadening can usually be circumvented by reacting an aliquot of the DME solution with an equal volume of a solution of potassium t-butoxide in DMSO. The radical anion can be favored by admission of a slight amount of oxygen. The usefulness of this technique can be seen in Figure 5.

One major disadvantage of this reaction in DME is that diesters containing aromatic rings give very poor results. The reasons why diesters I and II do not yield semidiones by this method are not well understood.

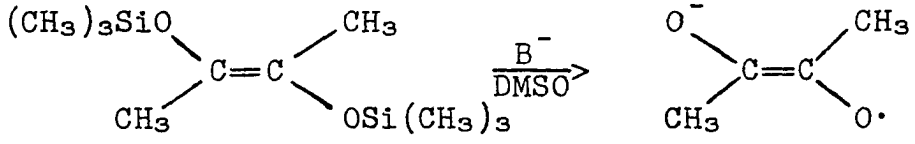


I



II

Since Mr. David Lawson[a] had shown that the bis(trimethylsiloxy)alkene IIIa could be converted to the semidione III in rather good yield simply by reaction with potassium t-butoxide in DMSO, this route was considered as an alternate method for generating bicyclic semidiones. From work



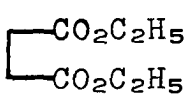
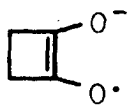
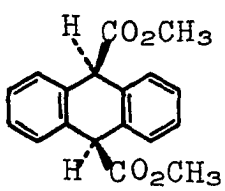
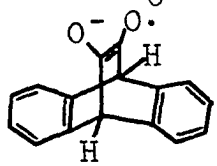
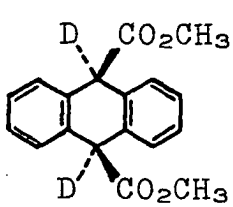
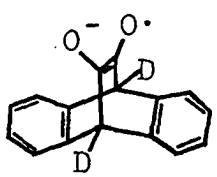
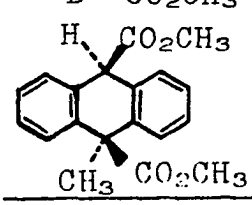
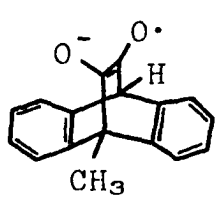
IIIa III

---

[a]Lawson, David, Chemistry Department, Iowa State University, Ames, Iowa 50010. Predoctoral research at Iowa State University. Private communication. 1968.

described in this thesis and that of other members of this research group, this method has been developed to the point that one can usually carry out a study on a semidione utilizing ten milligrams or less of the corresponding diester. A few examples of semidiones prepared by this method are listed in Table 3 and many other examples are integrated into the text of this thesis.

Table 3. Semidiones derived from the reaction of bis(trimethylsiloxy)alkenes with potassium t-butoxide in dimethyl sulfoxide

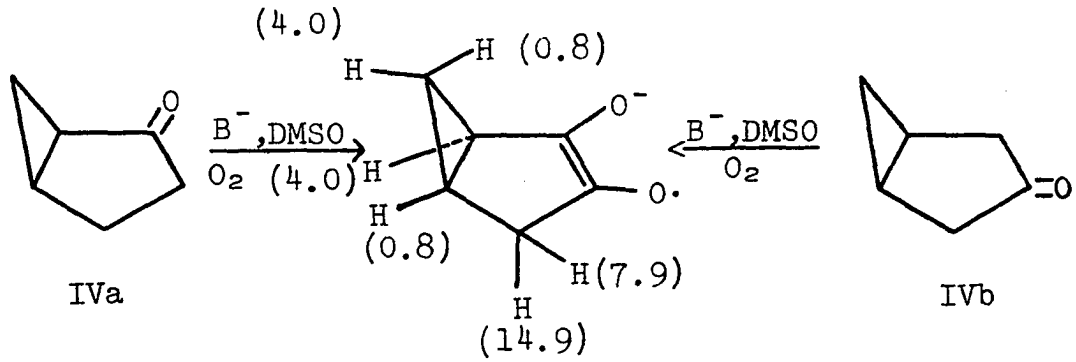
Diester	Semidione	Hyperfine Splitting Constants (gauss) Observed	Reported	Ref.
		13.85 (4H)	13.55 (4H)[a]	7
		0.15 (8H)[b]	0.15 (8H)	12
		0.15 (8H)[b]	---	--
		0.14 (11H)[b]	---	--

[a] In N,N-dimethylformamide.

[b] See Figure 6.

Bicyclo[3.1.0]hexane Semidiones

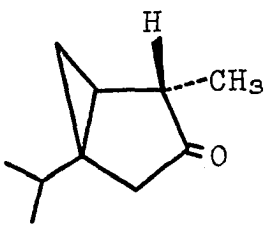
When either bicyclo[3.1.0]hexan-2-one (IVa) or bicyclo-[3.1.0]hexan-3-one (IVb) is oxidized in DMSO containing an excess of potassium t-butoxide, an ESR spectrum is observed which is attributed to the semidione IV (6, 37, 38). Specific deuteration and a large pattern of alkyl substitution allow assignment of the hyperfine splitting constants (hfsc) to the individual hydrogen atoms as shown in structure IV (hfsc in gauss) (37, 38).



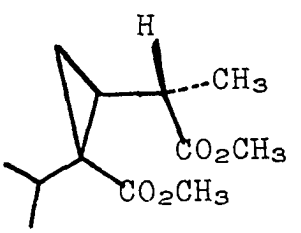
IVa IVb

IV

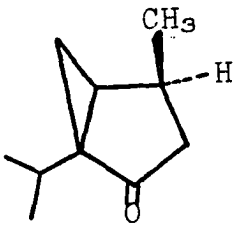
Early work in this system involved some naturally occurring terpenone derivatives. When thujone (Va) was oxidized in basic DMSO, the major radical had the following hfsc: a^H = 6.2, 4.8, 0.8 and 0.6 gauss (Figure 7a). The same radical (Figure 7b) can be obtained by the acyloin condensation of dimethyl homothujadicarboxylate (Vb). Similar oxidation of



Va



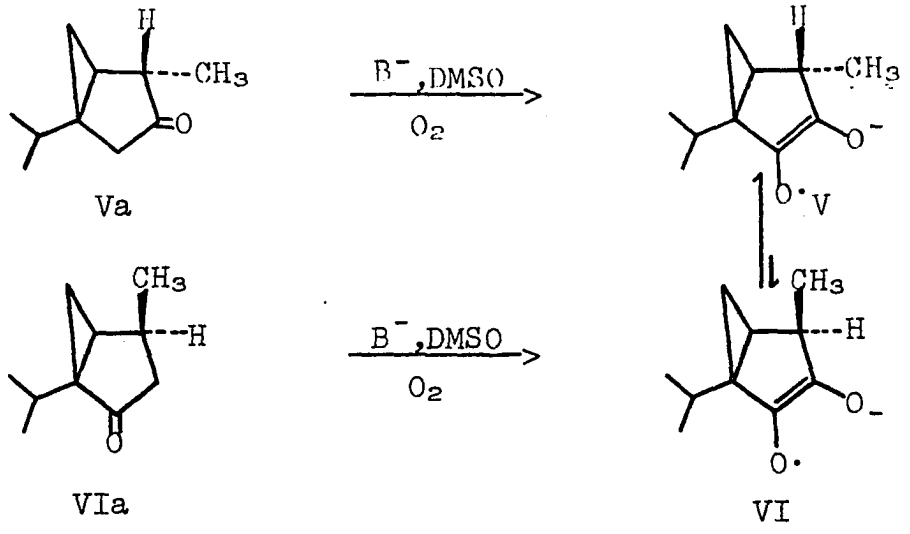
Vb



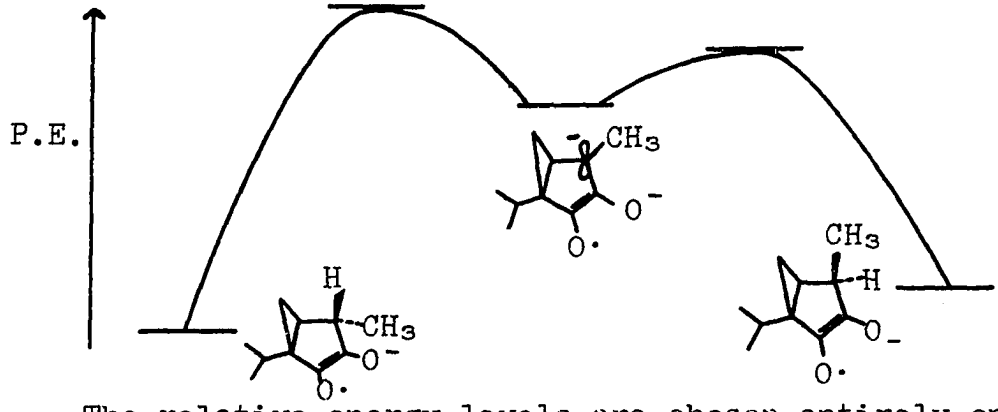
VIa

β-dihydroumbellulone (VIa) gave initially a radical with hfsc: a^H = 13.9, 4.9, 0.7 and 0.6 gauss. However, a new ESR signal soon appeared (Figure 8a) and began to increase in intensity at the expense of the original spectrum. After about three hours (with potassium t-butoxide in DMSO) this new radical accounted for about ninety percent of the total radical concentration (Figure 8b). This second radical had the same hfsc as the species obtained in the oxidation of thujone. Closer inspection of the spectrum from thujone revealed a minor radical whose hfsc were the same as in the original radical anion derived from β-dihydroumbellulone. Consequently, it was concluded that the processes in Chart III are involved. The rate of epimerization is slightly dependent upon the base (potassium, cesium, sodium or rubidium t-butoxide) and the solvent (DMSO, DMF or 80:20 DMSO:t-BuOH) employed. When the reaction is carried out in hexadeuteriodimethyl sulfoxide (d_6-DMSO), the same equilibria are observed, the largest hydrogen coupling in each case

Chart III

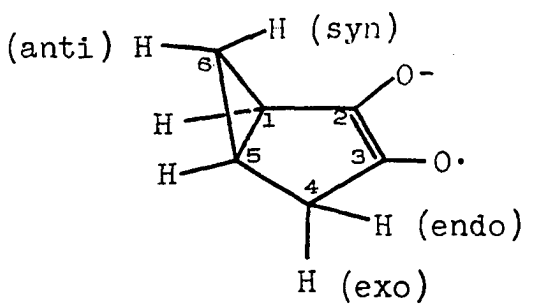


(a^H = 6.2 and 13.9 gauss) being replaced by a deuterium splitting (a^D = 0.95 and 2.2 gauss). The rate of deuterium exchange is much faster than the epimerization (see Figure 9). In order to explain the preceding facts, consider the following energy profile diagram:



The relative energy levels are chosen entirely on the basis of steric considerations. There is little doubt that semidione V is more stable than VI considering the interaction of the syn-6-hydrogen and the group at C-4 which is

cis to the three-membered ring. Approach of the base from the bottom of the molecule seems more favorable than from the more sterically crowded top side. From the principle of microscopic reversibility, the proton (or deuteron) should be added to the radical dianion from the bottom more easily than from the top. Hence VI should be the kinetically controlled product while V should be the thermodynamic product. This explains the rather rapid deuterium exchange but rather slow epimerization in the semidione derived from β-dihydroumbellulone.[a] The hfsc in these epimeric semidiones are consistent with those of other derivatives and provide the best evidence that the largest coupling in bicyclo[3.1.0]-hexane semidiones is due to the exo-4-hydrogen in IV. This



IV

is predicted from extended Hückel calculations (39).

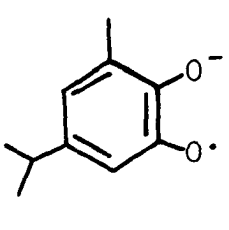
When the oxidation of β-dihydroumbellulone is effected with sodium t-butoxide in DMSO, sodium couplings (a^{Na} = 0.6

---

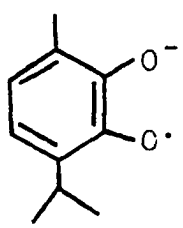
[a]This explanation was originally suggested by Dr. Walter S. Trahanovsky, Department of Chemistry, Iowa State University, Ames, Iowa 50010.

gauss; Figure 10) are observed. Sodium interactions can often be observed in acyclic semidiones, but are rarely detected in bicyclic systems.

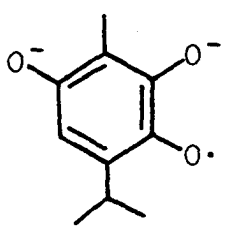
If excess air is added to the mixture of epimeric semidiones, a new ESR signal is observed (Figure 11; a^H = 3.0, 2.9, 0.6 (3H) and 0.5 gauss) which is assigned to the ortho-semiquinone VII. The mechanism of this rearrangement has been discussed (38, 40). The ESR spectrum of VII and the isomeric VIII would be essentially identical. However, VIII has been shown to be very readily oxidized to IX (Figure 12; a^H = 5.2 and 0.7 (4H) gauss) which could also be prepared from X, whereas further oxidation is not observed in this case.



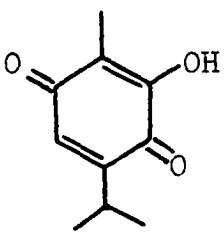
VII



VIII



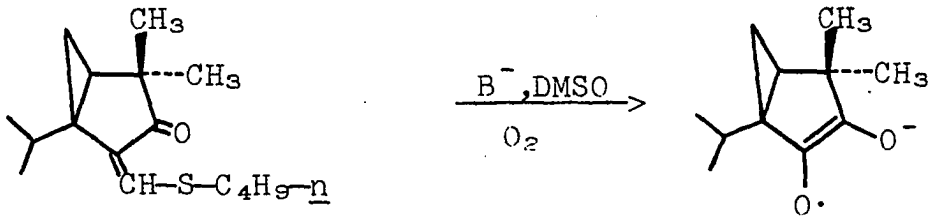
IX



X

In order to obtain a 4,4-dimethylbicyclo[3.1.0]hexane semidione, the n-butylthiomethylene blocking group (41) was employed to specifically methylate thujone. It was found that this derivative could be converted directly to the desired semidione by reacting with an excess of potassium t-butoxide in DMSO followed by admission of a trace of

oxygen.[a] The spectrum of XII (Figure 13) consists of a doublet (a^H = 4.9 gauss) due to the anti-6-hydrogen and a heptet (a^H = 0.4 gauss) due to six hydrogens which are approximately

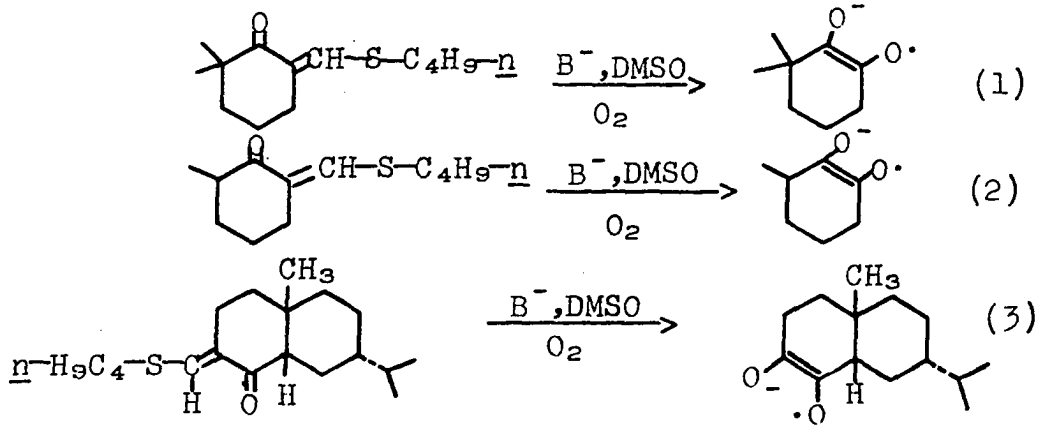


XI XII

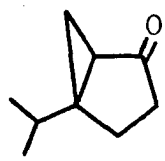
equivalent and are assigned to the exo-methyl at C-4, syn-6-hydrogen, the hydrogen at C-5, and the isopropyl tertiary hydrogen. Presumably there is restricted rotation of the isopropyl group and a conformation is favored in which appreciable spin density reaches the tertiary hydrogen.

---

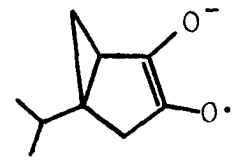
[a]This reaction was later shown to be a very good method for preparing semidiones in cases where the carbonyl group cannot enolize. For example , reactions 1 and 3 proceed very well to give good concentrations of radicals, while reaction 2 does not proceed to an appreciable extent (an acidic hydrogen is present).



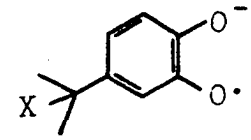
When sabina ketone (XIIIa) is oxidized in basic DMSO, the initial ESR spectrum is consistent with the bicyclic semidione XIII (Figure 15; a^H = 14.5, 8.2, 4.0, 3.7, 0.7 and 0.3 gauss). After four hours, this radical had decayed and another radical had appeared (a^H = 2.8, 0.9 and 0.4 gauss). When the solvent is d_6-DMSO, the large hydrogen splitting (a^H = 14.5 gauss) is rapidly replaced by a deuterium splitting (a^D = 2.2 gauss), while the second largest splitting (a^H = 8.2 gauss) is slowly replaced by a deuterium splitting (a^D = 1.3 gauss). After four hours this spectrum had disappeared



XIIIa



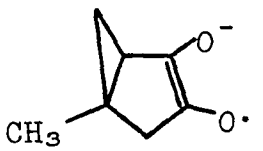
XIII



XIV

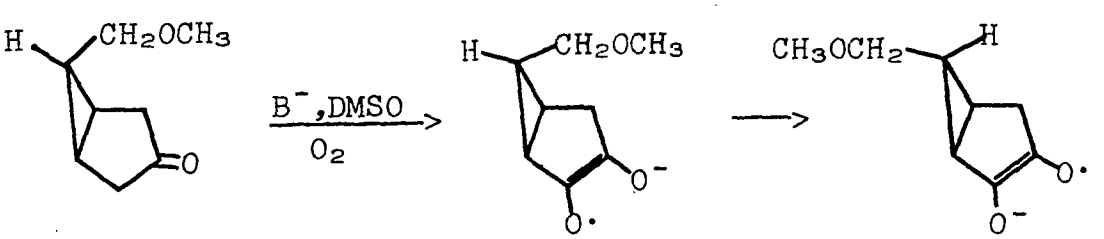
and a spectrum identical to the final one seen in ordinary DMSO was observed (Figure 16). The identity of this radical is not known, but the hfsc are characteristic of an ortho-semiquinone such as XIV (X is not hydrogen).

5-Methylbicyclo[3.1.0]hexan-2-one furnished the expected semidione XV (Figure 17; a^H = 14.20, 7.6, 3.8 and 3.8 gauss-fine structure not well resolved). This radical anion is formed in very low yield and decays rapidly.



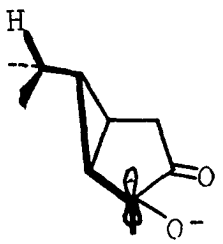
XV

In order to study the effect of substitution at C-6, ketone XVIa was prepared. Upon oxidation with potassium t-butoxide in DMSO, a very complex signal due to a mixture of radicals was observed initially, which, after about three hours, had simplified to a spectrum which could be attributed to a single semidione (Figure 18; a^H = 14.7, 7.8, 4.2, 0.8, 0.8 and 0.35 G). This semidione was assigned the rearranged structure XVII, on the basis of the hfsc which demand interaction by the two methylene hydrogens at C-7. This long range interaction has only been observed in bicyclo[3.1.0]-hexane semidiones in those cases in which the carbon-hydrogen



XVIa XVI XVII

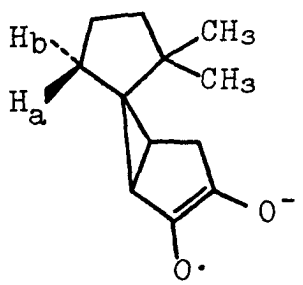
bond involved is oriented in a 2 1/2V arrangement (XVIII) with the p_z orbital of the π-system (37, 38).



XVIII

When XVIa is oxidized in the presence of cesium t-butoxide (a stronger base) in DMSO, the initial radical observed has the rearranged structure XVII. It was later shown (38, 40, 42) that this rearrangement occurs with other syn-6-alkylbicyclo[3.1.0]hexane semidiones and a mechanism for this isomerization has been discussed.

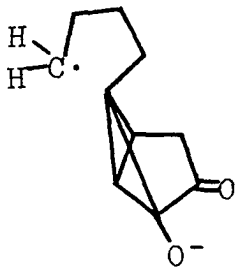
A good example of the effect of stereochemistry on the delocalization of spin from the π-system to a given hydrogen is provided by semidione XIX (Figure 19; a^H = 13.95, 7.20, 4.90, 0.85, 0.85 and 0.20 gauss) in which it is believed



XIX

that the hydrogens at C-7 are different (a^H = 0.85 and 0.20 gauss) since we expect the hydrogen at C-5 to be about 0.8 gauss. Careful inspection of molecular models reveals that

H_b is in a rather poor 2 1/2V arrangement with the p_z orbital whereas H_a is not so disposed. Thus we assign the larger splitting to H_b. There must be a second mechanism by which spin is transferred to C-7, possibly carbon-carbon homo-hyperconjugation (11) as in XIX'. Spin polarization can then



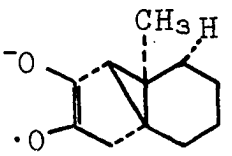
XIX'

lead to an equal free spin density on both hydrogens. The coupling constant of H_b must be made up of contributions from both the directed and homohyperconjugative mechanisms.

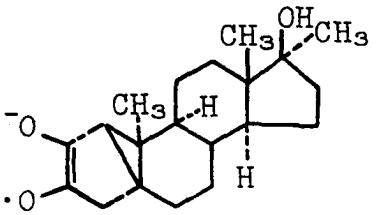
The importance of this "directed" coupling is emphasized by the fact that only one of the hydrogens at C-7 in XX[a] is observed (a^H = 1.0 gauss) and that a significant spin density reaches the corresponding hydrogen (a^H = 1.5 gauss) in the lumi-testosterone derivative XXI (37). Both of these hydrogens are in a 2 1/2V plan arrangement.

---

[a]Givens, Richard S., Department of Chemistry, University of Kansas, Lawrence, Kansas. 66044. Postdoctoral research at Iowa State University. Private communication. 1967.

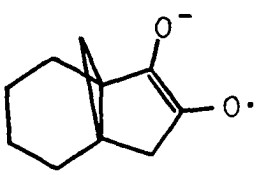


XX

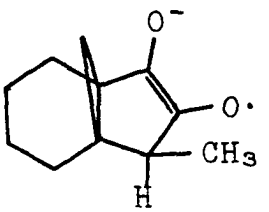


XXI

The tricyclic semidiones XXII and XXIII were prepared from the corresponding 2-ketones.



XXII

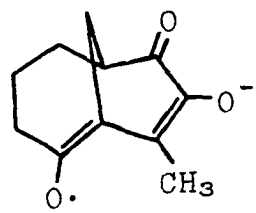


XXIII

The ESR spectrum of XXII demands interaction by seven hydrogens (Figure 20a; a^H = 14.4, 7.8, 4.4, 0.7 and 0.35 (3H) gauss), the two largest couplings being replaced by deuterium splittings (a^D = 2.2 and 1.2 gauss, respectively) when the reaction is carried out in d_6-DMSO (Figure 20b). A much lower concentration of XXIII was obtained and only the largest hfsc were determined (Figure 21a; a^H = 13.5 and 4.6 gauss). The largest hydrogen splitting was replaced by a deuterium splitting (a^D = 2.1 gauss) in d_6-DMSO (Figure 21b). In XXII, three of the hydrogens in the six membered ring have appreciable spin density, although one can only speculate as to which

three are involved.

The radical anion XXIII decays rather rapidly and when more oxygen is admitted, a new ESR spectrum is observed (Figure 22; a^H = 11.30, 4.85, 4.70, 1.10 (3H) and 0.67 gauss). This radical is not very stable but can be regenerated by the admission of additional oxygen (the solution is a brilliant green compared to the yellow color of the solution when XXIII was present). Without further study, one can only speculate upon the structure of this radical, but we feel that XXIV is a strong possibility. The reader is referred to the section



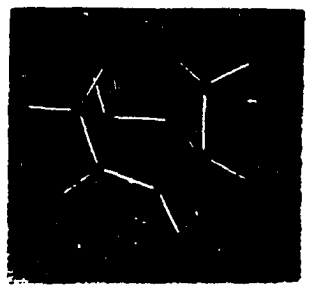
XXIV

on unsaturated semidiones in the appendix for a brief discussion of conjugated systems.

Bicyclo[4.1.0]heptane Semidiones

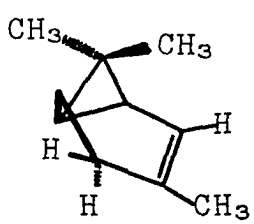
Upon inspection of Dreiding molecular models, it is observed that bicyclo[4.1.0]heptan-2,3-semidione can exist in either of two conformations, XXVa or XXVb, which might differ significantly in energy, depending upon the substitution.

XXVa

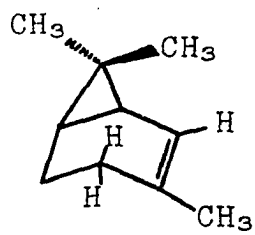


XXVb

Acharya (43) has studied the corresponding substituted olefin, 2-carene, and has shown by a NMR study of the anisotropic effect of the double bond on the syn-7-methyl group that the molecule exists in conformation XXIIa rather than in XXXIIb, in which maximum conjugation between the double bond and the cyclopropane ring is permitted (in XXXIIa the



XXXIIa



XXXIIb

π-orbitals of the double bond make an angle of about 15° with

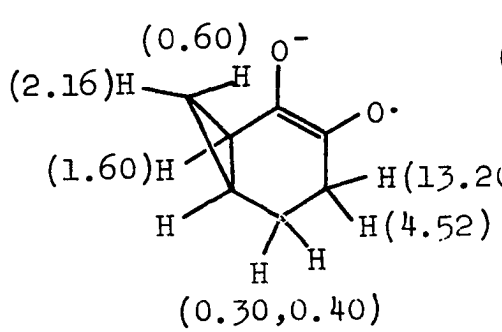
the plane of the three-membered ring, whereas in XXXIIb, this angle is approximately 0°). The separation between the syn-7-methyl and the 4-β-hydrogen was calculated to be only 0.2A° and this severe non-bonded interaction renders conformation XXXIIb unfavorable. This assignment is also supported by reactivity data (44).

The stereochemical orientations of the hydrogen at C-1 and the anti-7-hydrogen with respect to the π-system, differ significantly in the two conformations of the semidione. On the basis of the dihedral angle between the C_1-H bond and a p_z orbital of the π-system, H_1 should have a much larger coupling constant in conformation XXVa than in XXVb. A similar comparison at C-7 is not quite so obvious and was one of the major aims of this study.

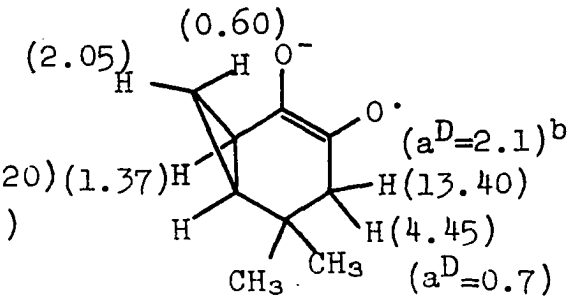
Several substituted bicyclo[4.1.0]heptane semidiones have been studied and the structures and assigned hfsc are shown in Chart IV.

An examination of the data in Chart IV reveals the constancy of the coupling constants assigned to the C-7 hydrogens throughout the series. Introduction of a methyl group at C-1 (XXVII and XXIX) increases the coupling constant of the anti-7-hydrogen slightly. This small effect was earlier observed in bicyclo[3.1.0]hexane semidiones and it is not known whether this is due to a slight change in geometry or to an electronic effect. It will be noted that

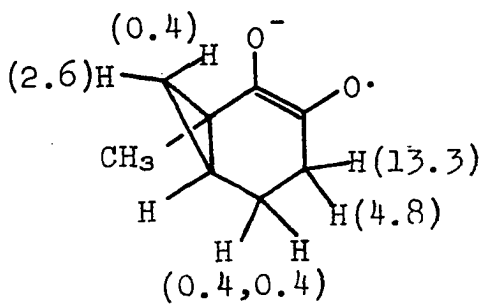
Chart IV[a]



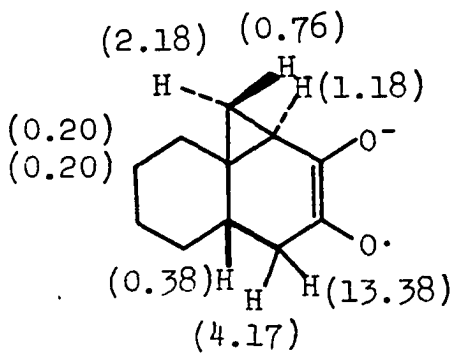
XXV



XXVI



XXVII



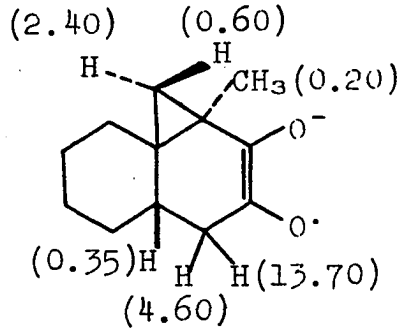
XXVIII

---

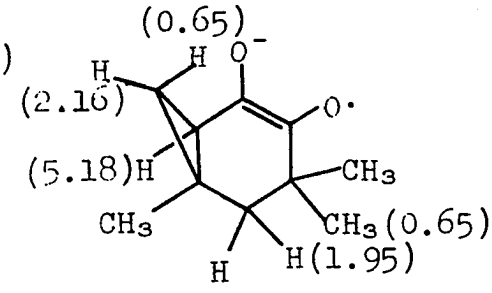
[a]The numbers in parentheses are the coupling constants (in gauss) assigned to the individual hydrogens. The given assignment of hfsc is that which seems most consistent with all the data. See Figures 23-31 for the ESR spectra.

[b]These values were obtained when the semidiones were prepared in d_6-DMSO.

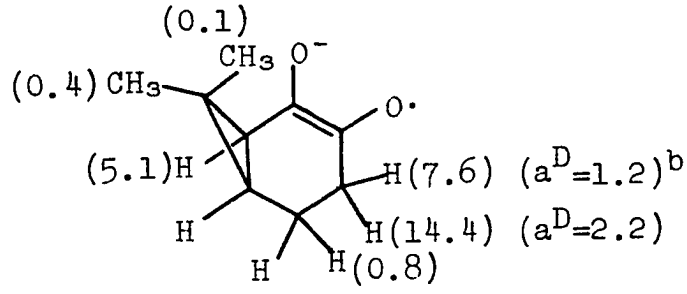
Chart IV continued



XXIX



XXX

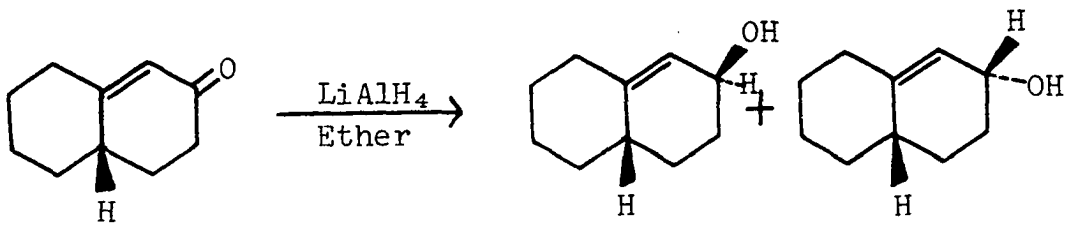


XXXI

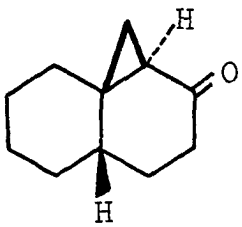
the anti-7-hydrogen in this system interacts only about one-half as strongly as the analogous anti-6-hydrogen in bicyclo[3.1.0]hexane semidiones.

The interaction of the hydrogen at C-1 remains rather constant in semidiones XXV, XXVI and XXVIII. The rather weak interaction of this hydrogen, coupled with the overall consistency of the coupling constants in XXV - XXIX, suggest that only the partial boat (type XXVb) conformation is significantly populated in these five semidiones. This frozen conformation would explain the large difference in the hfsc observed for the α-hydrogens, since it is predicted by the Heller-McConnell treatment (13) and has been demonstrated (4) that axial hydrogens give rise to larger coupling constants in cyclic semidiones than do equatorial hydrogens.

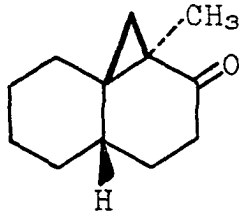
The assignment of stereochemistry in XXVIII and XXIX is based upon the report that lithium aluminum hydride reduction of $\Delta^{1,9}$-2-octalone gives primarily the cis allylic alcohol (45) as shown below.



Since the Simmons-Smith reaction is stereospecific with allylic alcohols (46), the major isomers, after oxidation to the ketones, should be XXVIIIa and XXIXa. Only one isomer was isolated by chromatographic methods in each case. If this



XXVIIIa

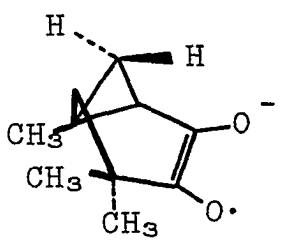


XXIXa

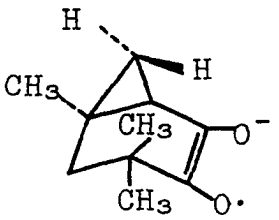
assignment of stereochemistry at C-7 is correct, Dreiding models suggest that the most stable conformation is that analogous to XXVb. This seems to provide additional support to the assigned conformational preference in XXV - XXIX.

Semidiones XXX and XXXI have ESR spectra (Figures 29 and 30) whose pattern of hfsc is much different than for semidiones XXV - XXIX. It should be noted that the interaction of the hydrogen at C-1 is much larger in these two radical anions and that the α-hydrogens in XXXI have coupling constants which differ significantly from those of XXV - XXIX. These facts almost demand that these two semidiones exist preferentially in conformations XXXa and XXXIa, rather than the alternates, XXXb and XXXIb, in which severe non-bonded interactions between the <u>syn</u>-7-group and the 4-β-

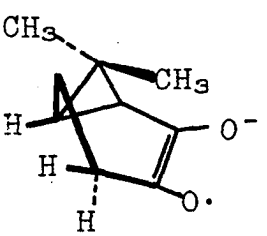
group exist, as in 2-carene.



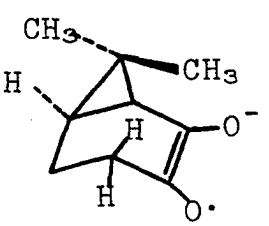
XXXa



XXXb



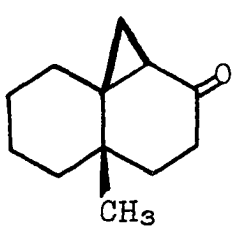
XXXIa



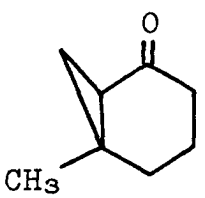
XXXIb

In XXX and XXXI only one of the hydrogens at C-5 interacts significantly with the free spin, presumably that hydrogen which is in a 2V arrangement with the p_z orbital, whereas in XXV and XXVII, couplings due to both of the C-5 hydrogens are observed. The coupling constant for the one hydrogen observed in XXX and XXXI is much larger than that seen for the C-5 hydrogens in XXV and XXIV.

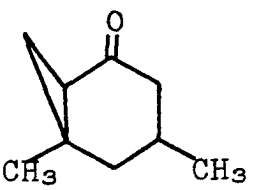
To further study this system, ketones XXXIII - XXXV were obtained. For reasons beyond our knowledge, none of these



XXXIII



XXXIV



XXXV

ketones could be oxidized to the semidione under standard conditions. Various oxidative studies on XXXIII failed to

yield a semidione with the desired skeleton.

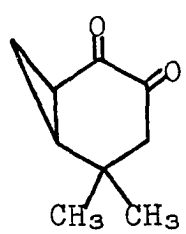
From the preceding results, one can conclude that bicyclo-[4.1.0]heptane-2,3-semidiones, in the absence of serious steric interactions, prefer to exist in the conformation (partial inverted boat) in which maximum conjugation exists between the π-system and the cyclopropane ring (conformation XXVb). However, with appropriate substitution at C-4 and C-7, one can reverse this conformational preference.

If rapid ring inversion were occurring in XXV, the α-hydrogens should become equivalent, but since they consistently differ by about a factor of three in XXV - XXIX, one must conclude that within the limits of our sensitivity, only conformation XXVb is populated. By the same token, only conformations XXXa and XXXIa are significantly populated in semidiones XXX and XXXI.

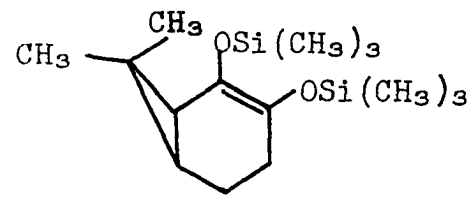
The rather constant value for the coupling constant of the anti-7-hydrogen in the two conformations is somewhat surprising in view of the large change in the coupling of the hydrogen at C-1. Since the ratios of the coupling constant of the anti-7-hydrogen to the syn-7-hydrogen in XXV and XXX are essentially equal, one must conclude that both the directed mechanism (homohyperconjugation) and the undirected mechanism (Fermi contact interaction) of transfer of free spin density are virtually unaffected by the small change in geometry. It should be realized, however, that the anti-7-hydrogen is in a very poor 2V plan arrangement

(i.e., the $H-C_7-C_1-C_2$ bonds and the p_z orbital at C-2 are far from being coplanar) in either conformation.

When the semidiones were prepared in d_6-DMSO, the α-hydrogens (methylene group) were exchanged with deuterium. Both α-hydrogens were exchanged very rapidly when the diketone XXVIa was reduced with the anion of propiophenone in



XXVIa

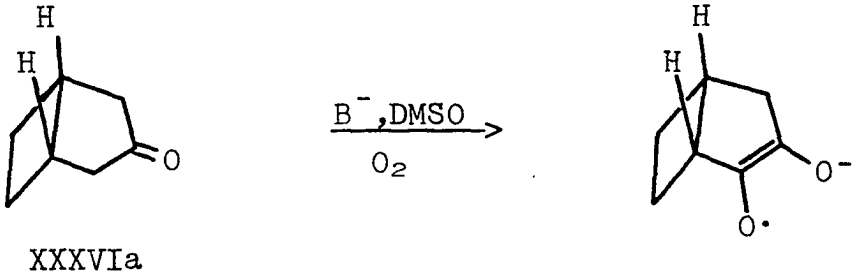


XXXIa

d_6-DMSO (Figure 25). In XXXI (prepared by reacting XXXIa with potassium t-butoxide in d_6-DMSO) the large hydrogen coupling (a^H = 14.4 gauss) was replaced within fifteen minutes by a deuterium splitting (a^D = 2.2 gauss) whereas exchange of the 7.6 gauss coupling was only partially complete after ten hours (see Figure 31). No exchange of the bridgehead hydrogen (at C-1) was noted in either case.

Bicyclo[3.2.0]heptane Semidiones

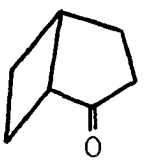
Russell, Talaty and Horrocks (6) in 1966 observed a very low concentration of a single radical anion, assumed to be XXXVI, when bicyclo[3.2.0]heptan-3-one (XXXVIa) was reacted with potassium t-butoxide and a trace of oxygen in DMSO. The ESR spectrum (a^H = 16.3, 10.7 and 10.7 gauss) was very poorly resolved but since the lines were very broad (the line-width was about 2 gauss), further long-range coupling was



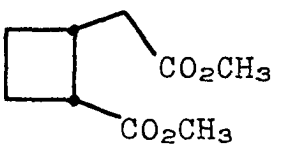
XXXVIa XXXVI

indicated. Due to the rigidity of this bicyclic system, we felt that a study of the long range interactions in a series of substituted bicyclo[3.2.0]heptane semidiones would be informative.

The first problem was to find a way to generate the parent semidione in higher yields. The isomeric ketone, XXXVIb, yielded extremely low concentrations of radicals. When cis-1-carbomethoxy-2-carbomethoxymethylcyclobutane (XXXVIc) was reacted with sodium-potassium alloy in DME, the desired radical was produced, but again, in such low yield that only the three large couplings could be resolved. When



XXXVIb

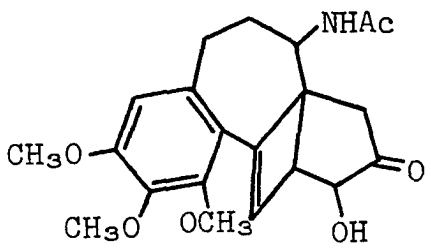


XXXVIc

the acyloin condensation was carried out in ether in the presence of chlorotrimethylsilane and this crude product was reacted with a solution of potassium t-butoxide in DMSO, the desired radical was not detected. Presumably the instability of the radical anion, rather than its formation, is the source of our problem.

Since a number of derivatives of the bicyclo[3.2.0]heptane system are known, we turned to a study of a series of these. The results are shown in Chart V. Only in those cases in which C-1 is substituted, can reasonable concentrations of semidiones be obtained from the ketones. Even with the 1-methyl substituent semidiones XLI and XLII could not be obtained directly from the 2-ketones, but were prepared from the corresponding diketones.

Reaction of lumiisocolchicine ketol (XXXVIIa) (47, 48) with potassium t-butoxide in DMSO gives the ESR spectrum in Figure 32 (a^H = 14.0, 11.4, 8.1 and 0.35 gauss). When this reaction is carried out in d_6-DMSO, the two largest couplings are replaced by deuterium couplings (Figure 33; a^H = 8.0

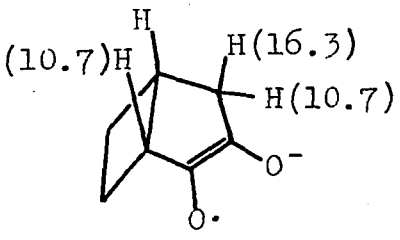


XXXVIIa

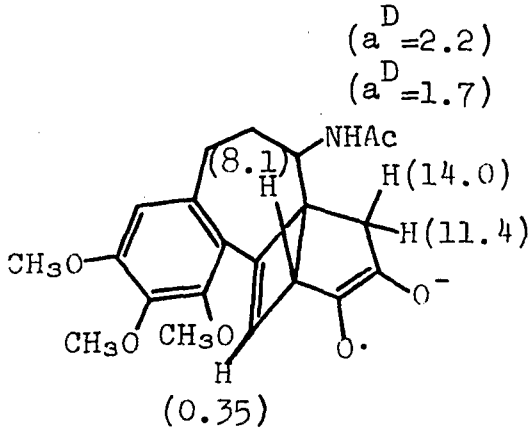
gauss; a^D = 2.2 and 1.7 gauss) whereas the 8.1 gauss hydrogen is not noticeably exchanged after twenty-four hours. Similarly, both of the large couplings in XLIII are replaced by deuterium couplings in d_6-DMSO (Figure 40; a^D = 2.1 and 1.7 gauss). In both XXXVII and XLIII, the hydrogen which interacts most strongly is exchanged at a much faster rate than the other one. Since the methylene hydrogens at C-4 are expected to exchange under these conditions, whereas the hydrogen at C-1 should probably not exchange (the α-bridgehead hydrogen does not exchange under these conditions in either bicyclo[3.1.0]hexane or bicyclo[4.1.0]heptane semidiones), the largest couplings must be due to the hydrogens at C-4. Comparison of XXXVII and XL shows the 8.1 gauss coupling is due to the hydrogen at C-1. Consequently, little imagination is required to assign the hfsc to the parent semidione as in Chart V.

The introduction of a double bond between C-6 and C-7 decreases the sum of the α-hydrogen coupling constants at C-4 by about ten per cent (the sums of the C-4 hydrogen

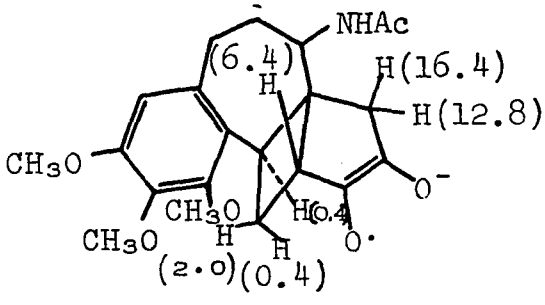
Chart V[a]



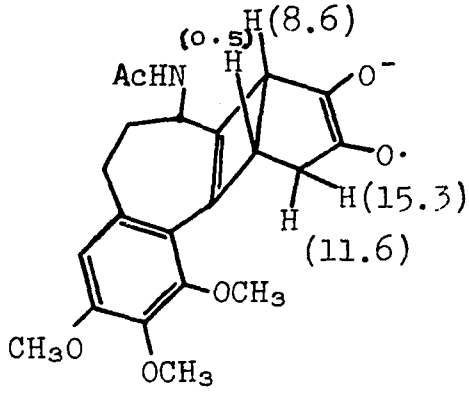
XXXVI



XXXVII



XXXVIII

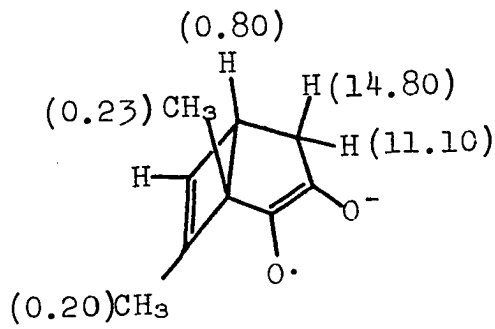


XXXIX

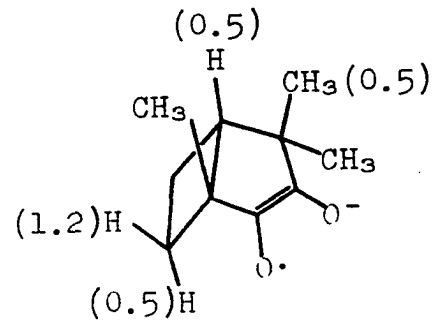
---

[a]The numbers in parentheses are the hfsc (in gauss) assigned to the particular hydrogen atoms. The assignments are those which seem most consistent throughout the series. See Figures 32-42 for the ESR spectra and method of preparing the semidiones.

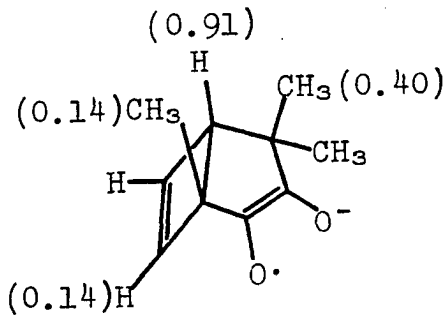
Chart V continued



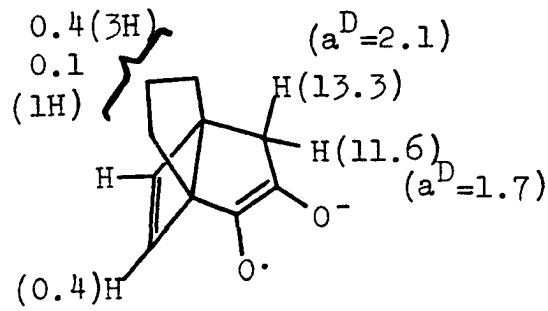
XL



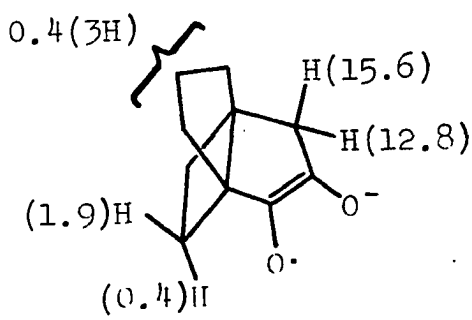
XLI



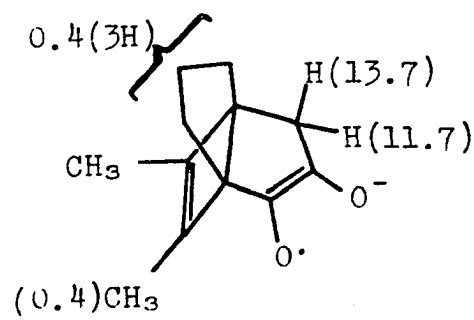
XLII



XLIII



XLIV



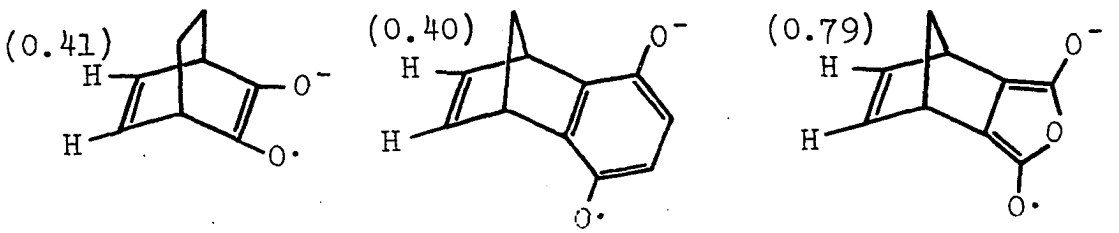
XLV

couplings in XXXVI, XXXVIII and XLIV are 27.0, 29.2 and 28.4 gauss, respectively, while the sums for the unsaturated derivatives XXXVII, XXXIX, XL, XLIII and XLIV are 25.4, 26.9, 25.9, 24.9 and 25.4 gauss, respectively). Since coupling due to the hydrogen (or methyl) at C-7 is observed, there may be appreciable spin density transmitted through C-7, thus lowering the spin density at C-4. This would explain the rather consistent decrease of both α-hydrogen coupling constants. Alternatively, the slight change in geometry created by the introduction of a double bond may account for the slight decrease in these coupling constants.

It seems apparent from the data in Chart V that the hydrogen at C-6 in the unsaturated compounds does not interact with the free spin density in the molecule. Semidione XXXIX has one small doublet coupling (Figure 35; $a^H = 0.5$ gauss) which must be assigned to the hydrogen at C-5. (This is about equal to the coupling of the C-5 hydrogen in bicyclo-[3.1.0]hexane semidione). Notice that similar couplings are also observed in the ESR spectra of XL, XLI and XLII, which, we believe, are due to the C-5 hydrogens rather than the C-6 hydrogens. The similarity of the coupling constants in XLIII and XLV (one hydrogen coupling in XLIII being replaced by a methyl coupling in XLV) is further evidence that there is not appreciable free spin density at C-6.

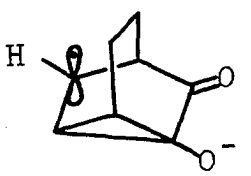
Coupling of vinyl hydrogens with a paramagnetic center

have been observed in similar cases such as XLVI (12), XLVII (49) and XLVIII (50).

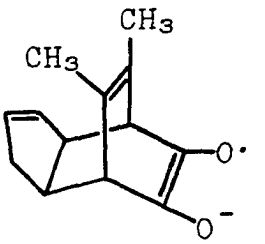


XLVI XLVII XLVIII

It was generally assumed that vinyl couplings arose through valence bond structures such as XLVIa in which 1,3 interaction is important.



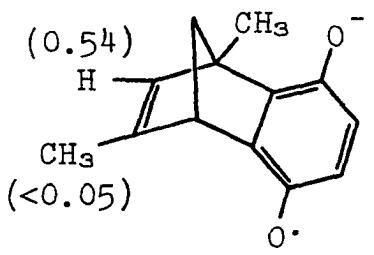
XLVIa



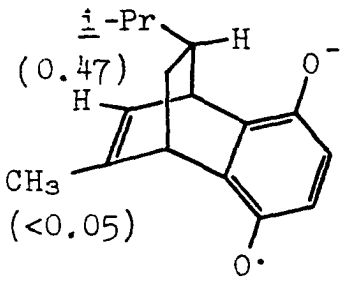
XLIX

This was supported by semidione XLIX (12) in which the methyl couplings ($a^{H}_{CH_3}$ = 0.48 gauss) were approximately equivalent to the vinyl hydrogen couplings in the parent semidione (XLVI). This should be true if both couplings are determined by the electron density, ρ_C^{π}, in the adjacent carbon π-orbital (51) as is the case in XLVIa. On the other hand, Kosman and Stock (51) have ruled out the importance of this mechanism

in the semiquinones, since in L and LI, the vinyl hydrogen is coupled with the free spin but coupling due to the methyl group cannot be detected. Thus, they postulate a spin



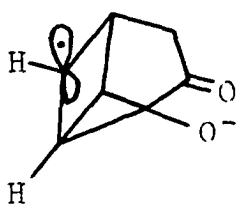
L



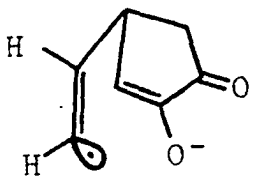
LI

polarization mechanism, either indirect (through bond) or direct coupling, which does not require electron density in a π-orbital, but allows the electrons in the vinyl carbon-hydrogen bond to become spin polarized by interaction with the spin density in the paramagnetic center.

Since our results indicate little spin density at C-6, the importance of valence bond structures such as LIIa can be neglected. If LIIb were important, one should expect to see

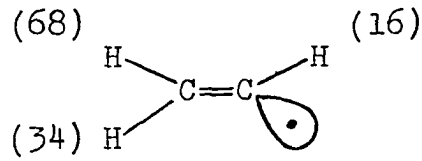


LIIa



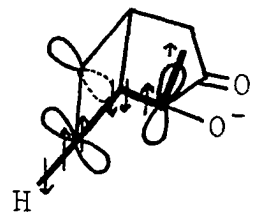
LIIb

coupling due to the C-6 hydrogen on the basis of the results obtained with the vinyl radical (52) whose hfsc (in gauss) are shown in LIII. Our data can be explained by assuming

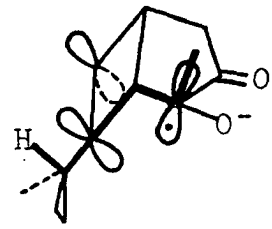


LIII

that spin polarization of the C_7-H bond takes place without effecting polarization at C-6. This could be due to a very directed mechanism (LIIc) whereby the π-orbital at C-7 aids spin polarization and is a special case of a 1.5V interaction.



LIIc

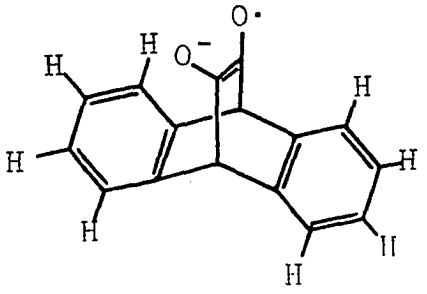


LIId

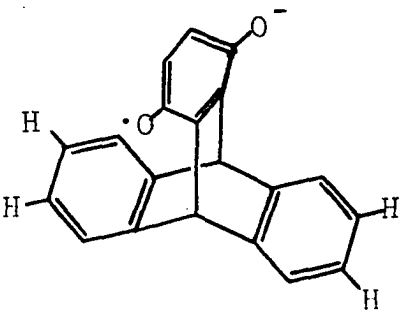
By this same argument, the methyl group at C-7 might be coupled by a mechanism (LIId) which is essentially a special case of a W-plan interaction.

It is very difficult to rationalize coupling by a vinyl methyl group in semidiones whereas the analogous coupling is not observed in the benzosemiquinones. Furthermore, other

differences between these two classes of radicals are observed. In LIV, coupling due to eight aromatic hydrogens is observed (12) whereas in LV, as well as in the corresponding semifuraquinones, only four aromatic hydrogens are coupled with the



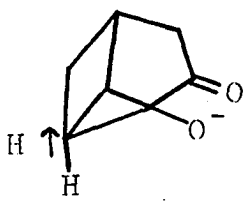
LIV



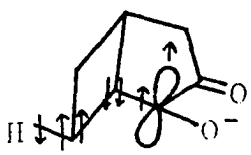
LV

free spin (53). It has been suggested (53) that the difference between the results for the semiquinones and semifuraquinones on the one hand and semidiones on the other hand, originates in their different symmetry characteristics of the highest occupied molecular orbitals.

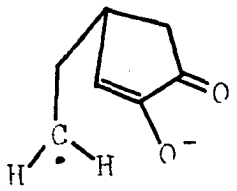
In the saturated bicyclo[3.2.0]heptane semidiones, a coupling is observed which ranges from 1.2 gauss (in XLI) to 2.0 gauss (in XXXVIII) which is attributed to the exo-7-hydrogen. This coupling is probably due to both a directed mechanism (such as XXXVId and/or Fermi contact interaction XXXVIe) and a hyperconjugative mechanism (XXXVIf), since a smaller coupling is observed which must be due to the endo-7-hydrogen. Only in XXXVIII is an additional small coupling



XXXVId



XXXVIe

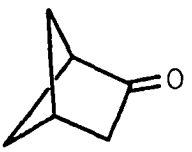


XXXVIf

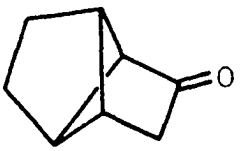
observed which must be due to the hydrogen at C-6. The assigned coupling of the exo-7-hydrogen is smaller than expected, but inspection of models reveal that the C_7-H bond is out of the plane defined by the C_7-C_1-C_2 bonds by about 45°, thus decreasing the effectiveness of this directed coupling.

Bicyclo[2.1.1]hexane Semidiones

Since the anti-7-hydrogen in bicyclo[2.2.1]heptane semidione and the anti-6-hydrogen in bicyclo[3.1.0]hexane semidione (both W-plan hydrogens) interact strongly with the unpaired spin, we felt that this type of long range coupling should be very effective in the heretofore unknown bicyclo-[2.1.1]hexane semidione. Initial experiments in which ketones LVIa and LVIIa were reacted with potassium t-butoxide and oxygen in DMSO failed to give the desired semidiones.



LVIa



LVIIa

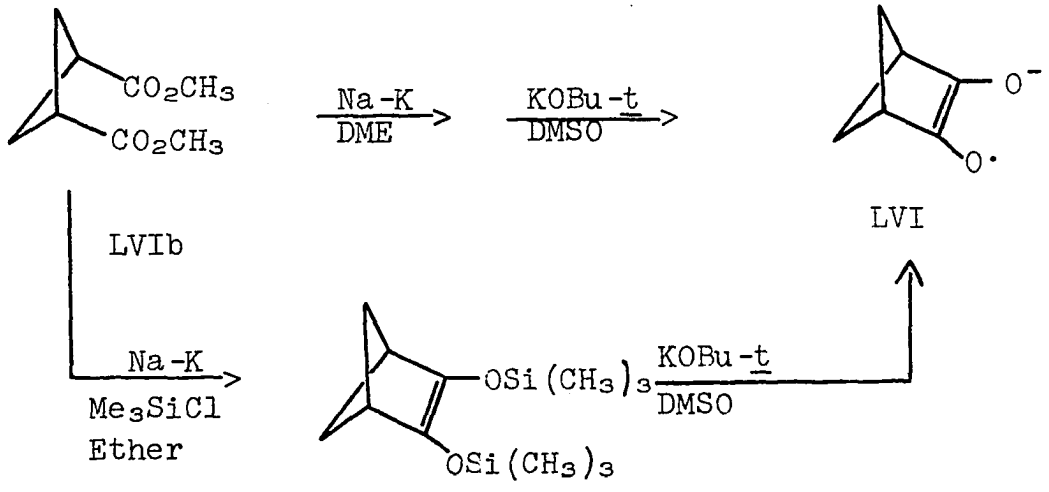
Since ketone LVIa is remarkably resistant to oxidation to the α-diketone[a] we turned to the acyloin condensation as a possible route into this system of semidiones.

Reaction of dimethyl cis-cyclobutane-1,3-dicarboxylate (LVIb) with sodium-potassium alloy in DME gave a radical with

---

[a]Bond, F. Thomas, Department of Chemistry, Revelle College, University of California, San Diego, La Jolla, California 92037. Research at Oregon State University. Private communication. 1968.

a poorly resolved ESR spectrum. When an aliquot of this solution was transferred under nitrogen to a degassed solution of potassium t-butoxide in DMSO, a well resolved ESR spectrum was obtained (Figure 43; a^H = 10.10 (2H), 0.40 (2H) and 0.25 (2H) gauss) in which every hydrogen in the molecule was coupled with the free spin. It was later shown that a



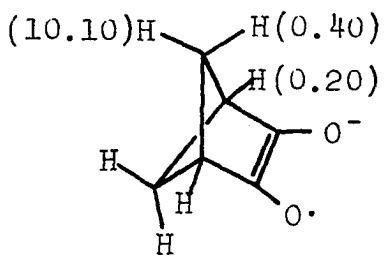
LVIc

very poor yield of the bis(trimethylsiloxy)alkene (LVIc) could be obtained by carrying out the acyloin condensation in ether at 0°C in the presence of chlorotrimethylsilane. This derivative (without purification) could then be converted to the same radical anion. The former method gave more satisfying results in this case.

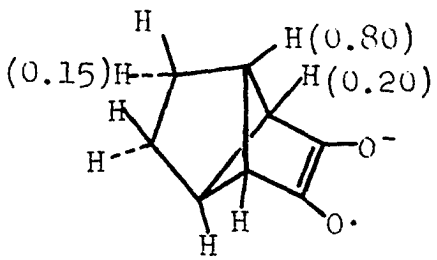
In order to substantiate our belief that the large triplet coupling was due to the anti-5- and -6- hydrogens, the derivatives in Chart VI were prepared from the corresponding

diesters via the bis(trimethylsiloxy)alkenes.

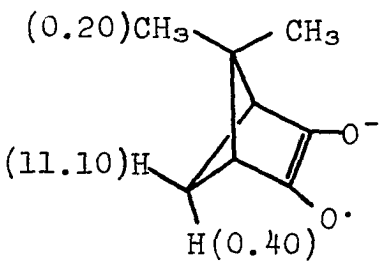
Chart VI[a]



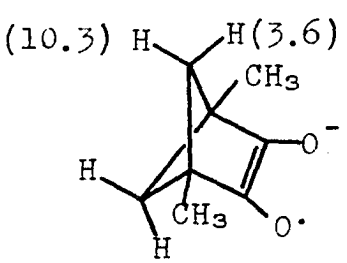
LVI



LVII



LVIII

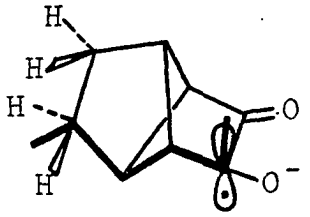


LIX

---

[a]The numbers in parentheses are the hfsc (in gauss) assigned to the particular hydrogen atoms. See Figures 43-46 for the ESR spectra.

The semidiones in this system decay rather rapidly (with the exception of LVIII which is quite stable) and one must record their spectra soon after generation. The study of LVII was complicated by its instability (half life of less than five minutes) and the appearance of another complex ESR spectrum (not well resolved but due to an unsymmetrical radical) superimposed upon the desired spectrum. The reported hfsc for this radical anion were extracted from the initial spectra of three separate reactions (see Figure 46). It is very clear from this semidione that the largest couplings in bicyclo[2.1.1]hexane semidiones do arise from the anti-5- and anti-6-hydrogens. The γ-hydrogens in LVII are coupled very weakly with the free spin and provide another example of 2.5V coupling. Since the γ-hydrogens are rigidly held in an unfavorable geometry for this type of interaction, the

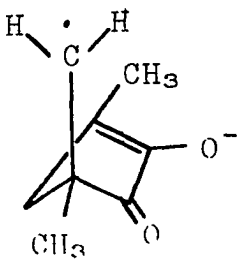


LVII

coupling is expected to be quite small. Note that one of the methyl groups in LVIII is coupled weakly with the free spin, presumably the anti-5-methyl, by this same type of mechanism.

The assignment of the small couplings in LVI and LVII to the α- and β-hydrogens is based only upon intuition and could possibly be reversed. It is clear that the bridgehead (α) hydrogens in LVIII are less than 0.05 gauss. Since the bridgehead hydrogens lie almost in the nodal plane of the π-system, they are expected to be quite small. Thus we assign the smaller triplet in each case (in LVI and LVII) to the bridgehead hydrogens.

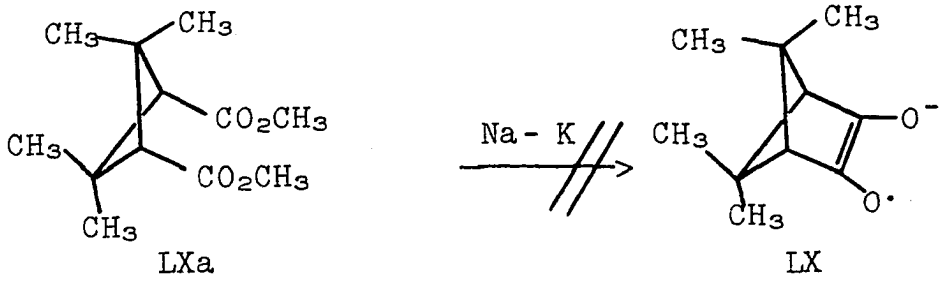
The large couplings in LVI, LVIII and LIX (assigned to the anti-5- and -6-hydrogens) are rather constant. However, the couplings assigned to the syn-5- and syn-6-hydrogens vary considerably. We find it very difficult to explain the roughly ten-fold increase in this coupling constant upon introduction of methyl groups at C-1 and C-4 (i.e., in LIX). After an inspection of molecular models, one can conclude that the steric interactions seem to be decreased by decreasing the C_6-C_1-C_2 and C_5-C_1-C_2 angles in LIX, thus bringing C-5 and C-6 in closer proximity to the site of maximum free spin density. As a result of the increased strain energy of the molecule, hyperconjugation (as in LIXa) becomes more important, thus placing more spin density at C-5 and C-6 than in the parent semidione. Hence one expects the syn-5- and -6-hydrogens to interact more strongly with the free spin in this semidione. Since the coupling constant of the anti hydrogens must have contributions from both



LIXa

directed and hyperconjugative type mechanisms, the directed interaction must be decreased by about the same amount as the increase in effectiveness of the hyperconjugative mechanism, so that we observe little overall change in the anti hydrogen couplings. A study of semidiones LVI and LIX with carbon-13 enrichment at C-5 and C-6 would be helpful in exploring the above facts.

The acyloin condensation of dimethyl cis-2,2,4,4-tetramethylcyclobutane-1,3-dicarboxylate (LXa) does not lead to the



LXa LX

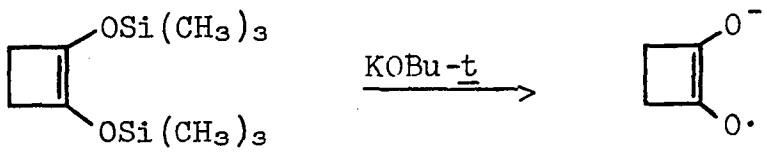
bicyclo[2.1.1]hexane semidione LX. Inspection of models show that the interactions of the anti methyl groups in LX are very, very severe and this semidione should be very unstable. When the diester was reacted with sodium-potassium alloy in ether

in the presence of an excess of chlorotrimethylsilane and the crude product was reacted with a solution of potassium t-butoxide in DMSO, a rather intense ESR signal was observed (Figure 47; a^H = 9.1 (2H) gauss). When the crude product was reacted with potassium t-butoxide in d_6-DMSO, the hydrogens were completely replaced by deuteriums within 20 minutes (Figure 48; a^D = 1.40 (2D) gauss). This radical must be a monocyclic semidione with two acidic α-hydrogens. Analysis of the crude acyloin product by vapor phase chromatography revealed the presence of at least five products which were not readily separable. This reaction was not pursued further, since we feel the bicyclo[2.1.1]hexane system was not an intermediate, but the products arose from free radical reactions of the ketyl originally formed. This is supported by the fact that when mixtures of the cis and trans diesters are employed, both diesters are consumed in the reaction.

Substituted Cyclobutanesemidiones

A rather extensive study of a series of fused ring cyclobutanesemidiones was undertaken for three primary reasons: (1) the cyclobutene ring is very rigid and thus should remain virtually unchanged upon substitution; (2) the geometry of this spin label seems ideal for the transmission of long-range coupling; and (3) these semidiones are very accessible through the *in situ* acyloin condensation of the corresponding 1,2-dicarboxylic esters (29).

Cyclobutanesemidione can be conveniently prepared by reacting the bis(trimethylsiloxy)alkene LXIa (24) with a solution of potassium *t*-butoxide in DMSO (Figure 49; a^H = 13.85 (4H) gauss). As can be seen from Table 3, the hfsc

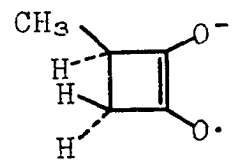


LXIa LXI

are slightly larger in DMSO than the values reported (7) for the radical anion in N,N-dimethylformamide. When LXIa is reacted with a solution of potassium *t*-butoxide in d_6-DMSO, the hydrogens are slowly exchanged by deuteriums (Figure 50; a^D = 2.15 (4D) gauss). Cyclobutanesemidione has been studied over the temperature range -90 to +70°C and no significant temperature effect upon the hfsc was observed (7). The

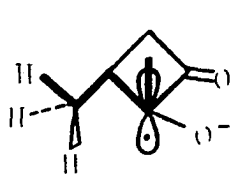
four carbon atoms must be planar or the inversion frequency is extremely high. The former assumption certainly seems more reasonable.

Introduction of a methyl group at C-3 (LXII) doesn't

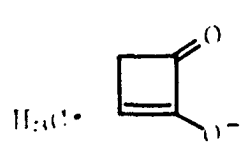


LXII

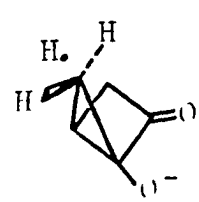
change the hfsc of the α-hydrogens very much (Figure 51; a^H = 14.8, 14.8 and 12.8 gauss). These hfsc should be compared with 14.4 gauss couplings of LXI in DME (see Table 1), in which case we see that the methylene hydrogen couplings in LXII are essentially unchanged while the methine hydrogen coupling is decreased slightly. The very surprising fact is that the methyl hydrogens are not coupled significantly ($a^H_{CH_3}$ <0.1 gauss) even though it seems LXIIa should be a favorable W-plan interaction. This result seems to suggest that mechanisms such as carbon-carbon hyperconjugation (LXIIb) and homohyperconjugation (LXIIc) are also not important in this case.



LXIIa

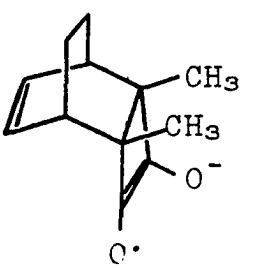


LXIIb



LXIIc

When the cyclobutanesemidione spin label is incorporated into a bridged ring system, a wealth of long-range interactions are observed. A series of semidiones in which this spin label is incorporated into a bicyclo[2.2.2]octane ring system is summarized in Chart VII. Note that the hfsc assigned to the α-hydrogens remain rather constant over a small range (slightly higher in DME for LXIII-LXVI). The ESR spectrum of LXXII (Figure 61) demonstrates that the

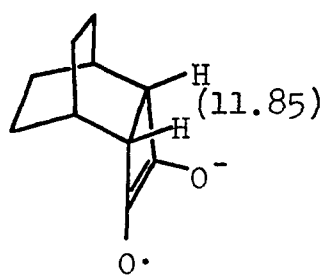


LXXII

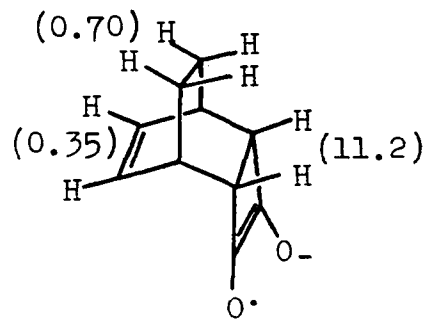
large triplet in semidiones LXIII-LXXI is due to the cyclobutane hydrogens, since it does not appear in the spectrum for LXXII (the spectrum is rather complex with at least 15 lines with an approximately equal spacing of 0.22 gauss).

In semidione LXIII, the only hfsc which can be resolved are due to the α-hydrogens although the lines are broadened, perhaps indicating further small coupling (Figure 52). Therefore, we must conclude that the long-range coupling shown in LXIIIa (2.5V interaction) must be rather small (<0.1 gauss). It is interesting to note that this coupling is not observed in the isomeric semidione LXXIII either

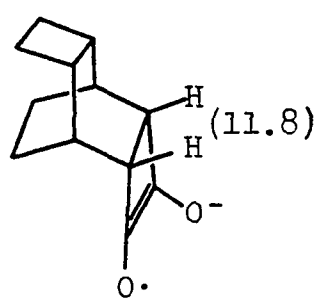
Chart VII[a]



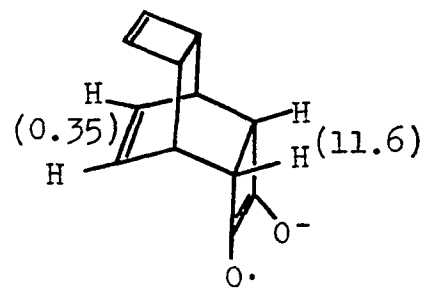
LXIII



LXIV



LXV

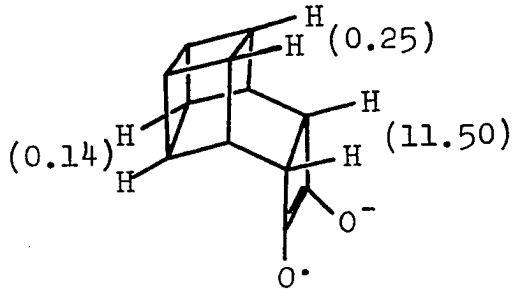


LXVI

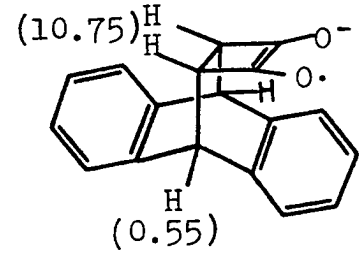
---

[a]The numbers in parentheses are the assigned hfsc in gauss. Semidiones LXIII-LXVI were prepared by the in situ acyloin condensation in DME; LXVII-LXXI were prepared by reacting the crude bis(trimethylsiloxy)alkenes with potassium t-butoxide in DMSO. See Figures 52-60 for the corresponding ESR spectra.

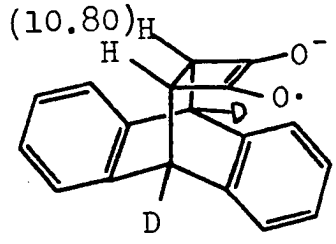
Chart VII continued



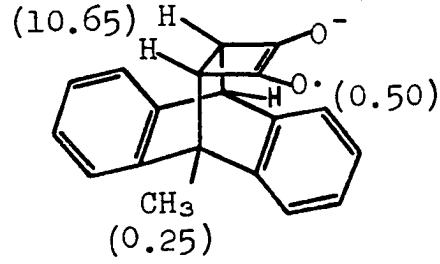
LXVII



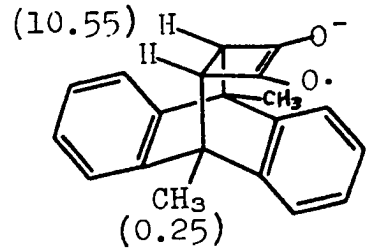
LXVIII



LXIX

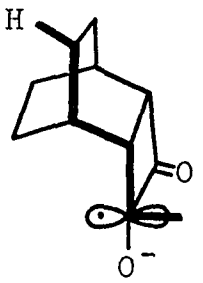


LXX

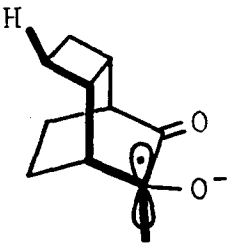


LXXI

(Figure 62; a^H = 2.3 (2H) gauss). Introduction of a double



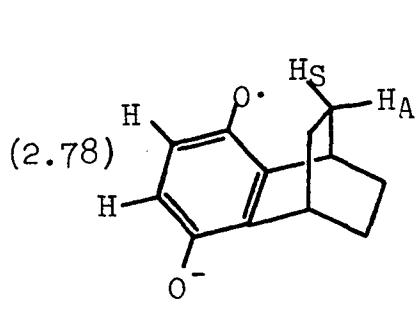
LXIIIa



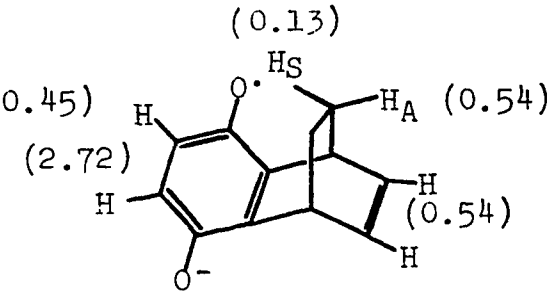
LXXIII

bond into the system (as in LXIV) adds two new coupling constants (see Figure 53). In the case of 7,8; 9,10-dibenzotricyclo[4.2.2.$0^{2,5}$]deca-7,9-diene-3,4-semidione (LXVIII), it has been shown by deuterium and alkyl substitution (LXIX-LXXI) that the hydrogens at C-1 and C-6 are coupled with the free spin. Since methyl groups at C-1 and C-6 are also coupled ($a^H_{CH_3} = 1/2\ a^H_H$), there must be appreciable spin density at these two positions. This is supported by the observation of a carbon-13 coupling assigned to these carbons (C-1 and C-6) (see section in Appendix concerning carbon-13 couplings).

We are therefore faced with the problem of assigning the smaller hfsc in LXIV. Kosman and Stock (54) have shown that in the semiquinone LXXIV the <u>syn</u> hydrogens (H_S) are not coupled with the free spin and only the four <u>anti</u> hydrogens (H_A) are observed, whereas in the unsaturated derivative LXXV, in addition to the two <u>anti</u> hydrogens, two other pairs of hydrogens were coupled. These were assigned

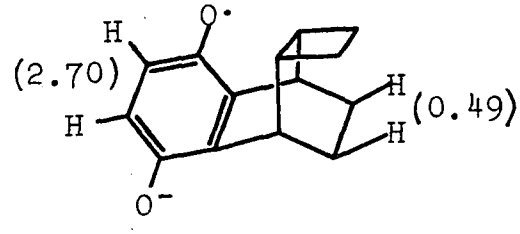


LXXIV

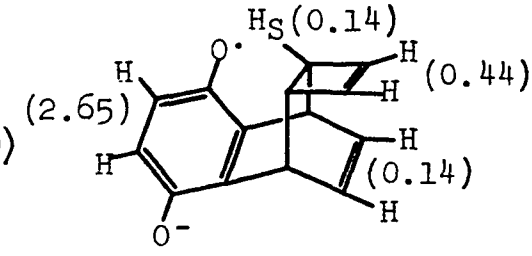


LXXV

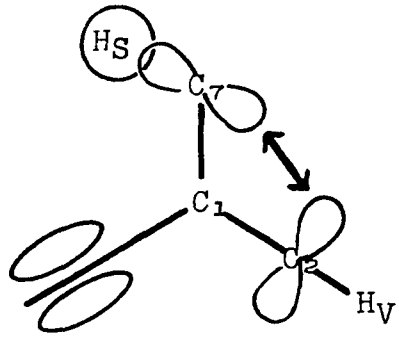
to the vinyl and <u>syn</u> hydrogens. When the derivatives LXXVI and LXXVII are compared one observes a similar trend. They suggest the spin density may be propagated through one π-orbital to the rear lobe of the <u>syn</u> proton (as in LXXVIII) or to another π-orbital (both pairs of vinyl



LXXVI



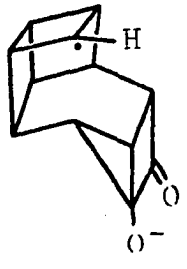
LXXVII



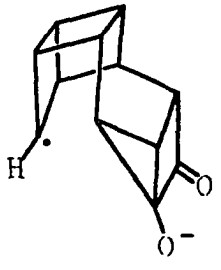
LXXVIII

hydrogens in LXXVII are coupled with the free spin). This same type of mechanism had earlier been postulated by Nelsen and Trost (50b). Later data by Kosman and Stock (51) tend to cast doubt upon this mechanism since a vinyl methyl group does not interact appreciably with the free spin (see page 44). Since the geometry of the ring fusion of the spin label into the bicyclo[2.2.2]octane ring is much different in the quinones and the semidiones, it may not be valid to compare them. Semidione LXVI (the analog of semiquinone LXXVII) has only one resolvable coupling, in addition to the α-hydrogens, and this we assign to the vinyl hydrogens. This seems to support the premise that the bridgehead C-1 and C-6 hydrogens are not interacting and the couplings in LXIV should be assigned as in Chart VII. It was also assumed for the quinones LXXVI and LXXVII that the bridgehead hydrogens did not interact. However, we can certainly not rule out the possibility that one triplet in the ESR spectrum of LXVI arises from the C-1 and C-6 hydrogens.

The assignment of hfsc in LXVII is rather uncertain. One can imagine that homohyperconjugation (LXVIIa and LXVIIb)

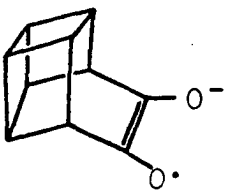


LXVIIa



LXVIIb

might be more important in this highly strained system than in the corresponding tricyclic systems. The value for a^{H}_{syn} in semidione LXXIX is also higher than in any of the other saturated bicyclo[2.2.2]octane semidiones (Reference 12; a^{H} = 0.53 (4H) and 0.09 (2H) gauss).

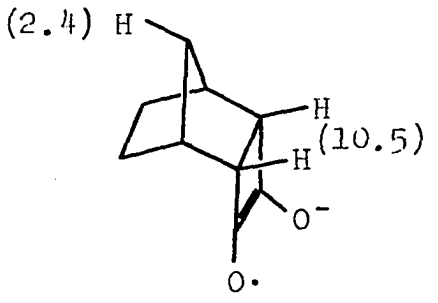


LXXIX

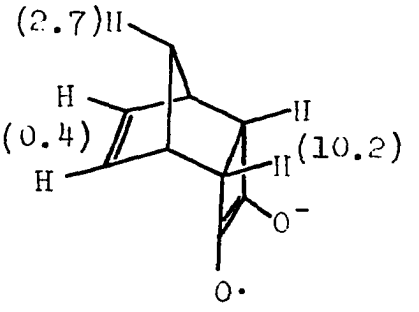
When the β-carbons of cyclobutanesemidione are incorporated into a bicyclo[2.2.1]heptane nucleus, very interesting long-range couplings are observed. Some of these results are summarized in Chart VIII.

Again, in these systems, the α-hydrogen couplings remain almost constant throughout the series. Inspection of the data in Chart VIII reveals strong 2.5V interactions by the γ-hydrogens which are so disposed. In semidione LXXX the only coupling other than that due to the α-hydrogens is assigned to the anti-9-hydrogen (a 2.5V interaction) while in LXXXI an analogous 2.5V coupling is observed, as well as another coupling which is assigned to the vinyl hydrogens. That this coupling is due to the anti-9-hydrogen is demonstrated by its absence in semidione LXXXII. The

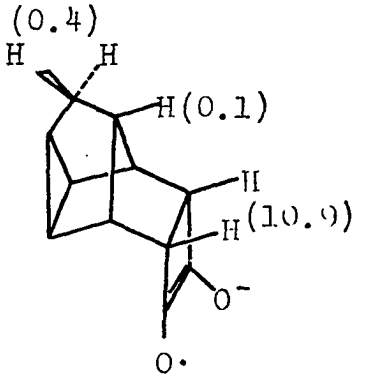
Chart VIII[a]



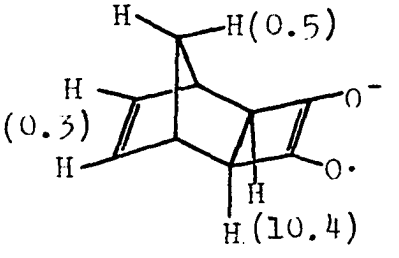
LXXX



LXXXI



LXXXII

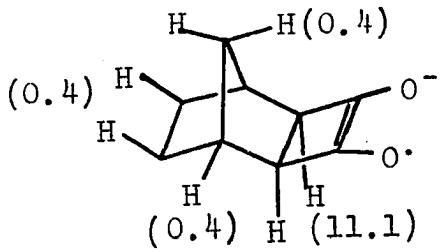


LXXXIII

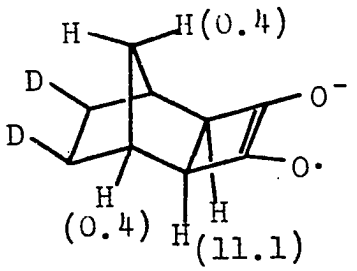
---

[a]The numbers in parentheses are the assigned hfsc (in gauss). All the semidiones were prepared by the in situ acyloin condensation with sodium-potassium alloy in DME. See Figures 63-69 for the corresponding ESR spectra.

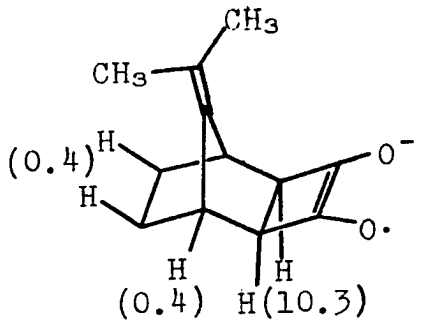
Chart VIII continued



LXXXIV



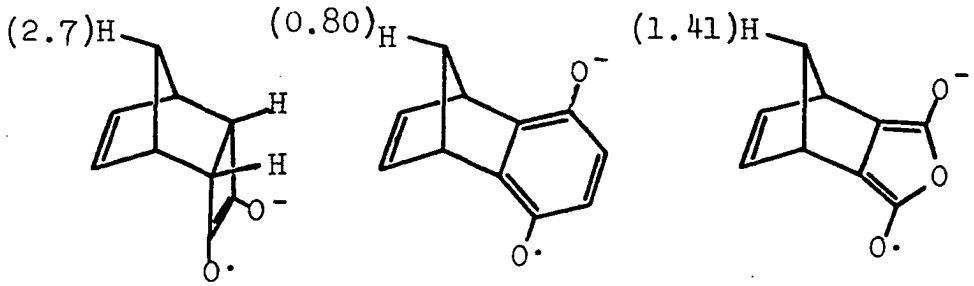
LXXXV



LXXXVI

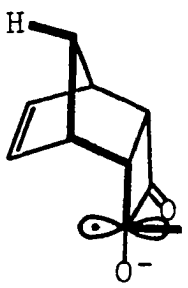
assignment of the two smallest hfsc in LXXXII are not definite, but the 0.4 gauss coupling is most likely due to the indicated pair of hydrogens (a 3V interaction).

A comparison of this stereoselective long-range coupling in the semidiones with that in the corresponding semiquinones (49) and semifuraquinones (50) shows that it is more favorable in the former case. This becomes obvious when LXXX, XLVII and XLVIII are compared. If the same mechanism of



LXXX XLVII XLVIII

coupling is involved, this demonstrates the very stereoselective nature of the W-plan coupling. In LXXX, this <u>trans</u> (or 2.5V) arrangement of bonds is very favorable,

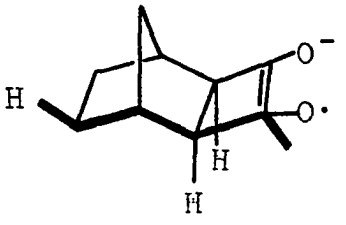


LXXX

whereas in XLVII and XLVIII, the indicated hydrogen is

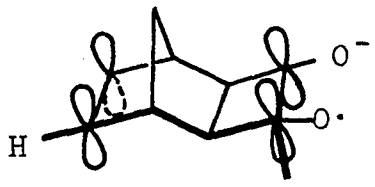
essentially in the nodal plane of the spin label and would be expected to interact more weakly.

When the cyclobutanesemidione spin label is exo in the tricyclo[4.2.1.$0^{2,5}$]nonane system as in LXXXIV, the exo hydrogens at C-7 and C-8 are oriented in a 2.5 V fashion and



LXXXIV

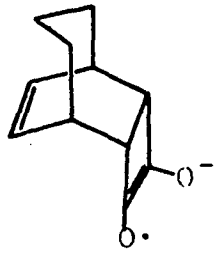
indeed these hydrogens are coupled weakly with the free spin. This is easily demonstrated by replacing these exo hydrogens by deuteriums (LXXXV) in which case this coupling is not detected (compare Figures 67 and 68). One of the hydrogens at C-9 in LXXXIII-LXXXV interacts weakly (note the absence of this coupling in LXXXVI). The assignment of this coupling to the syn-9-hydrogen is only tentative. The vinyl hydrogens in LXXXIII are coupled as in the endo compounds. This coupling must be transmitted through bonds due to the stereochemistry of the molecule. We feel this is further evidence for the importance of a modified 2 V interaction (as discussed for the bicyclo[3.2.0]hept-6-en-2,3-semidiones). Still an additional small coupling (2H) is observed in LXXXIV-LXXXVI which must be due to either the endo hydrogens at C-7 and C-8 or the



LXXXIII

pair of hydrogens at C-1 and C-6. Since both pairs of hydrogens are observed in the corresponding semifuraquinones (50a), we cannot make a definite assignment from our data.

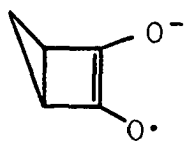
Incorporation of this spin label into other rigid polycyclic systems could prove valuable in the assignment of stereochemistry in the system. One other system of this type which was examined is LXXXVII (Figure 70; a^H = 12.3 (2H) gauss - remainder of spectrum very complex) which has several small couplings but was not studied further.



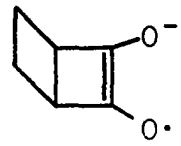
LXXXVII

We next turned to a study of bicyclic semidiones with the spin label in a four-membered ring. All attempts toward the preparation of LXXXVIII and LXXXIX were unsuccessful

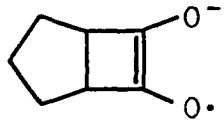
(see section in Appendix on Rearrangements Under Acyloin Conditions). On the other hand, higher homologs such as XC[a]



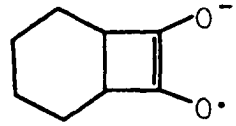
LXXXVIII



LXXXIX



XC



XCI

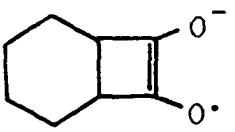
and XCI are readily available via acyloin condensations of the appropriate dicarboxylic esters. A series of derivatives of XCI has been studied and these are summarized in Chart IX.

An inspection of Dreiding models shows that the most favorable conformation for XCI should be XCIa or XCIb. One could imagine either conformation being highly favored (>95%) or a rapid equilibration between the two conformers

---

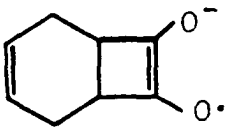
[a]Keske, R. G., Department of Chemistry, Iowa State University, Ames, Iowa 50010. Predoctoral research at Iowa State University. Private communication. 1968.

Chart IX[a]



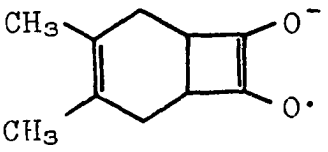
13.50G(2H)
0.50G(2H)
0.25G(2H)

XCI



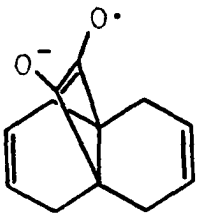
13.50G(2H)
0.60G(2H)
0.35G(2H)

XCII



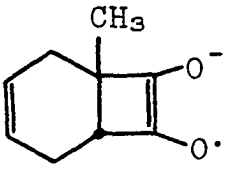
13.0G(2H)
0.7G(2H)

XCIII



0.90G(2H)
0.45G(6H)
0.12G(4H)

XCIV

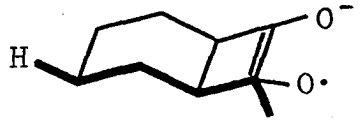


13.5G(1H)
1.2G(1H)
0.4G(2H)
0.2G(3H)

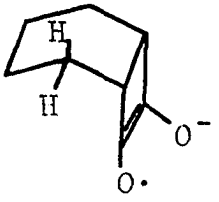
CXV

---

[a]Semidiones XCI and XCII were prepared by the *in situ* acyloin condensation in DME, XCIII and XCV by reaction of the pure bis(trimethylsiloxy)alkenes with potassium *t*-butoxide in DMSO, and XCIV by the reaction of the α-hydroxy ketone with potassium *t*-butoxide in DMSO. See Figures 1 and 71-74 for the ESR spectra.



XCIa



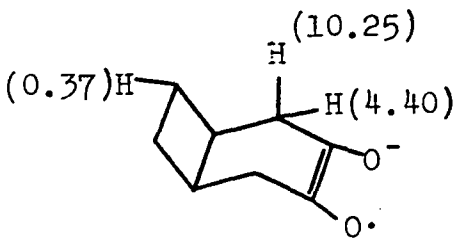
XCIb

with each being about equally populated. Conformation XCIb can be intuitively ruled out by the data in Chart IX since in this conformation, one pair of β-hydrogens (at C-2 and C-5) is in a very good W-plan and we would expect to see a larger coupling than observed, whereas the other β-hydrogens are in the nodal plane of the π-system and should not interact. One would not expect long range coupling from the γ-hydrogens in this conformation (compare with LXIII). If rapid ring inversion were occurring, the two pair of β-hydrogens should become equivalent (unless one conformation were slightly favored). If conformation XCIa were highly favored (>95%), one might expect to see coupling by two of the β-hydrogens and the two <u>exo</u> hydrogens at C-3 and C-4 (2.5V arrangement).

The data in Chart IX seems most consistent with conformation XCIa. The consistent value of the second largest hfsc (the largest hfsc is due to the α-hydrogens) throughout the series suggests a single conformation. In XCII and XCV, the 0.35 and 0.4 gauss couplings are probably due to the vinyl

hydrogens and can be accounted for by the modified 2V interaction (discussed earlier for the bridged analogs), since in XCIII, only two pair of hydrogens interact with the free spin. The 1-methyl substituent in XCV reduces one of the β-hydrogen interactions to near 0 gauss while the other β-coupling is increased to 1.2 gauss and suggests a twisted boat conformation. Finally in XCIV, every hydrogen in the molecule is coupled with the free spin.

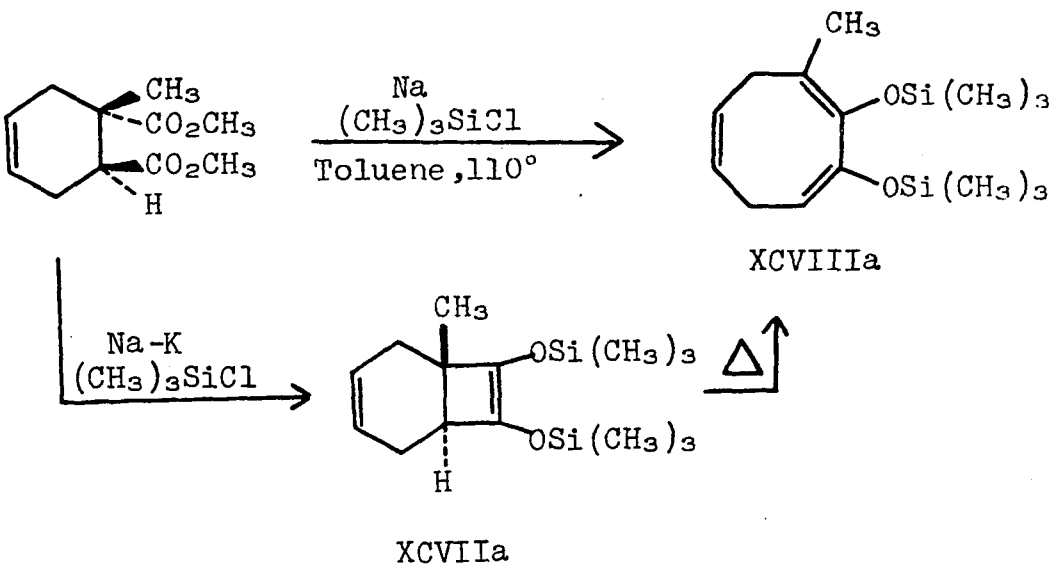
It is very interesting to compare the hfsc of XCI with those of the isomeric semidione XCVI (Figure 75; a^H = 10.25 (2H), 4.40 (2H) and 0.37 (2H) gauss) which is assigned the



XCVI

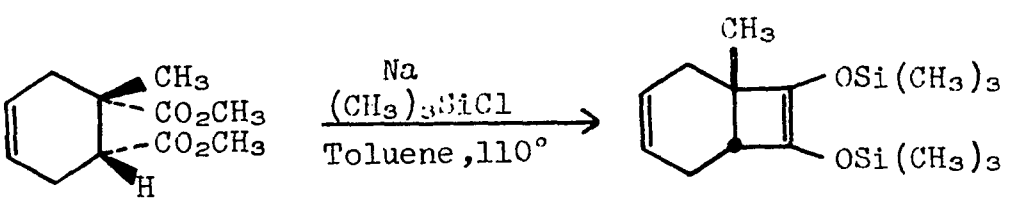
same type of conformation based upon the size of the smallest coupling constants. The largest couplings are due to the α-hydrogens since these are replaced by deuterium couplings in d_6-DMSO.

Bloomfield (26) has shown that the acyloin condensation of dimethyl trans-1-methylcyclohex-4-ene-1,2-dicarboxylate yields the cyclooctatriene derivative XCVIIIa under normal conditions (sodium in refluxing toluene) in the presence of chlorotrimethylsilane, whereas under milder conditions (sodium-potassium alloy in ether at 0°) the cyclobutene derivative XCVIIa is formed, but is unstable thermally and slowly isomerizes to XCVIIIa. The cis-cyclobutene derivative XCVa is thermally stable.



XCVIIIa

XCVIIa



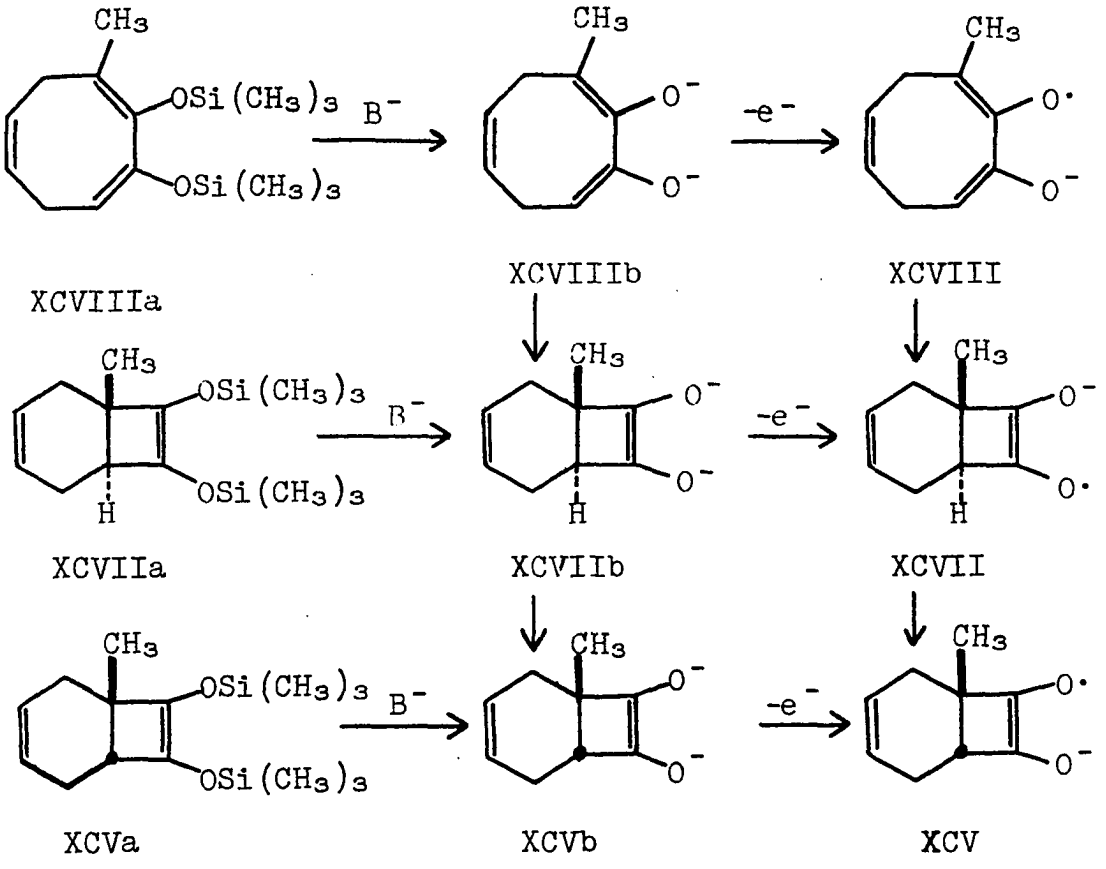
XCVa

When either XCVIIa or XCVIIIa was reacted with potassium t-butoxide in DMSO, an ESR spectrum was obtained which was identical to that obtained from XCVb (semidione XCV). When these reactions were carried out in d_6-DMSO, the α-hydrogen was exchanged by deuterium in each case, but at different rates. With XCVIIa as the substrate, 75% exchange had occurred within 15 minutes and the exchange was about 95% complete within 40 minutes (Figure 77), when the semidione was prepared from XCVa, only 55% hydrogen-deuterium exchange had occurred after 240 minutes (Figure 76). Finally, when the semidione was prepared from XCVIIIa, about 40% exchange had occurred after 45 minutes (Figure 78). A much lower concentration of radicals was obtained from XCVIIa and XCVIIIa than from CXVa.

These results lead us to postulate the reactions in Chart X. A very fast hydrogen-deuterium exchange must occur in either XCVIIb or XCVII. Most of the ring closure from XCVIIIa must proceed through XCVIIIa to yield the trans-bicyclo-[4.2.0]octane derivative (this conrotatory process is allowed by orbital symmetry). Since neither semidione XCVII nor XCVIII is observed by ESR, their concentrations must be very low in comparison to that of XCV.

The isomerization of XCVII to XCV and the rapid hydrogen-deuterium exchange observed in the semidiones derived from XCVIIa and XCVIIIa must mean that XCVII is much more acidic

Chart X



than XCV. On the other hand, the exchange may be occurring <u>via</u> the corresponding diketones which should be in equilibrium with the radical anions, with the <u>trans</u> diketone being much more acidic than the <u>cis</u> isomer. Relief of steric strain upon ionization of the α-hydrogen could explain this enhanced acidity in either case.

When semidiones XCI and XCII were generated in d_6-DMSO, the two α-hydrogens were slowly exchanged. Typical results are shown in Table 4.

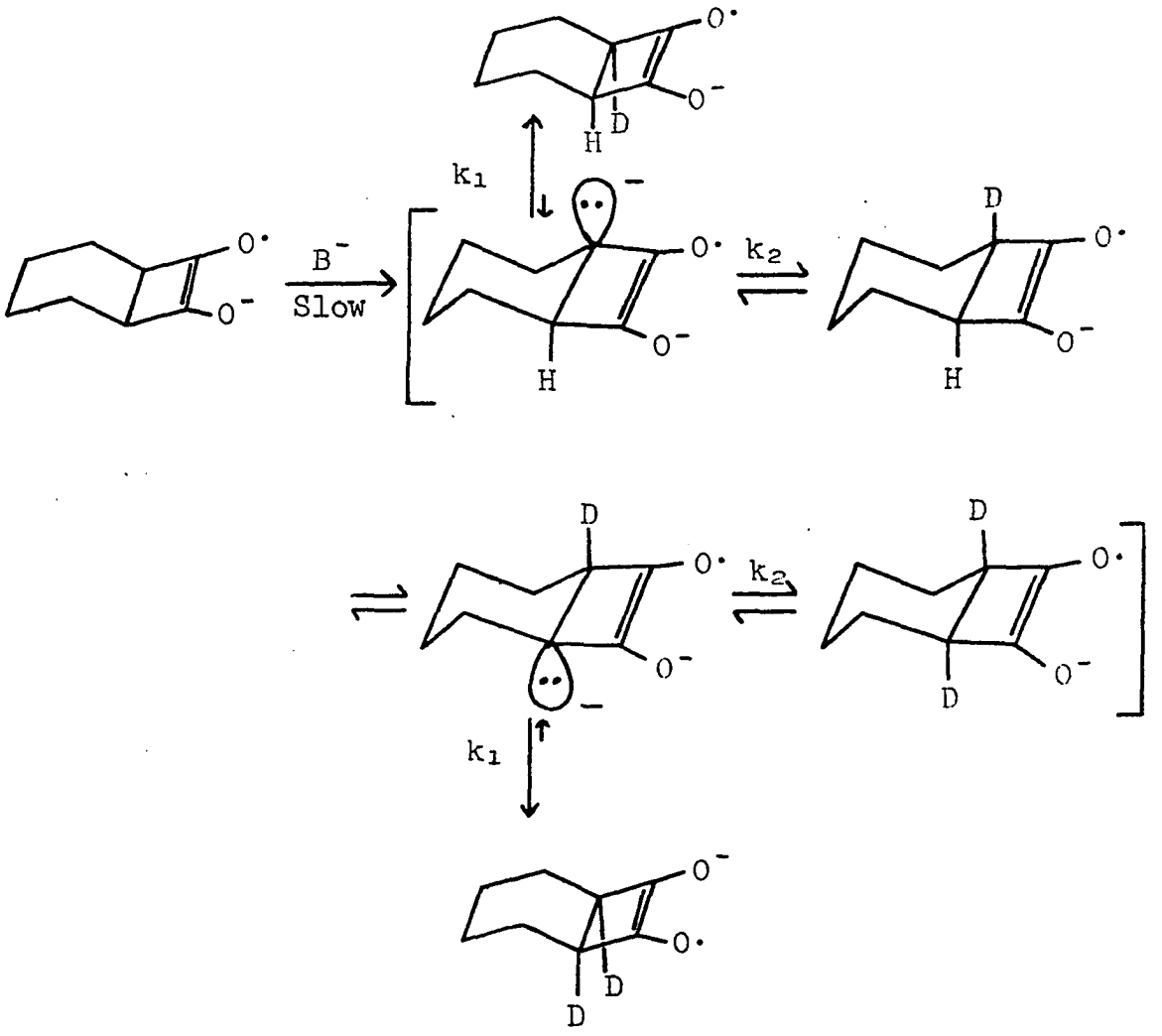
Table 4. Hydrogen–deuterium exchange in semidiones XCI and XCII in d_6-DMSO [a]

Semidione	Time (min)	% d_0	% d_1	% d_2
XCI	30	61	11	28
XCI	60	46	9	45
XCI	150	14	8	78
XCII	450	50	18	32
XCII	1380	37	19	44

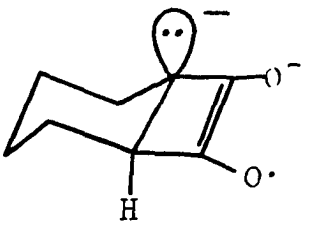
[a] 0.2 M potassium t-butoxide, 0.1 M bis(trimethylsiloxy)-alkene.

It should be noted from Table 4 that in both XCI and XCII, the concentrations of dideuterated species are greater than the corresponding monodeuterated species (even early in the exchange process). Therefore, we must seek a mechanism which explains a two-deuterium exchange which is faster than a single deuterium exchange in a given radical anion. One possibility is that the trans isomers are involved in a sequence such as that shown in Chart XI. If k_2 is at least five times as large as k_1 and if the trans semidione is at least ten times as acidic as the cis-isomer, the results in Table 4 are easily explained. The fact that the α-hydrogens in XCII are exchanged more slowly than in XCI seems

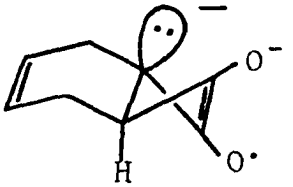
Chart XI



consistent with the strain energies of the corresponding radical dianions XCIa and XCIIa. Again, we cannot rule out the involvement of the corresponding diketones in this exchange.



XCIa

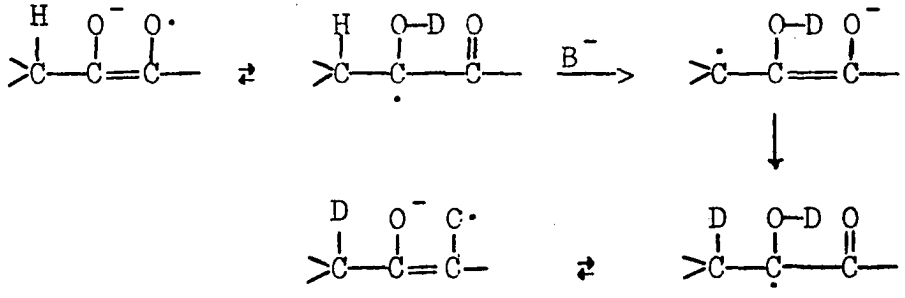


XCIIa

Exchange of the α-hydrogens occurs much faster in d_6-DMSO which is slightly wet.[a] In fact, the rate of exchange in XCI and XCII is increased by at least a factor of 100 when 2% (by volume) deuterium oxide is added to the solution. A preferential two deuterium exchange could not be detected in this case since the reaction had progressed to a late stage before the spectrum could be recorded. Likely mechanisms for this exchange are shown in Chart XII. The experimental evidence does not allow us to distinguish between the two mechanisms.

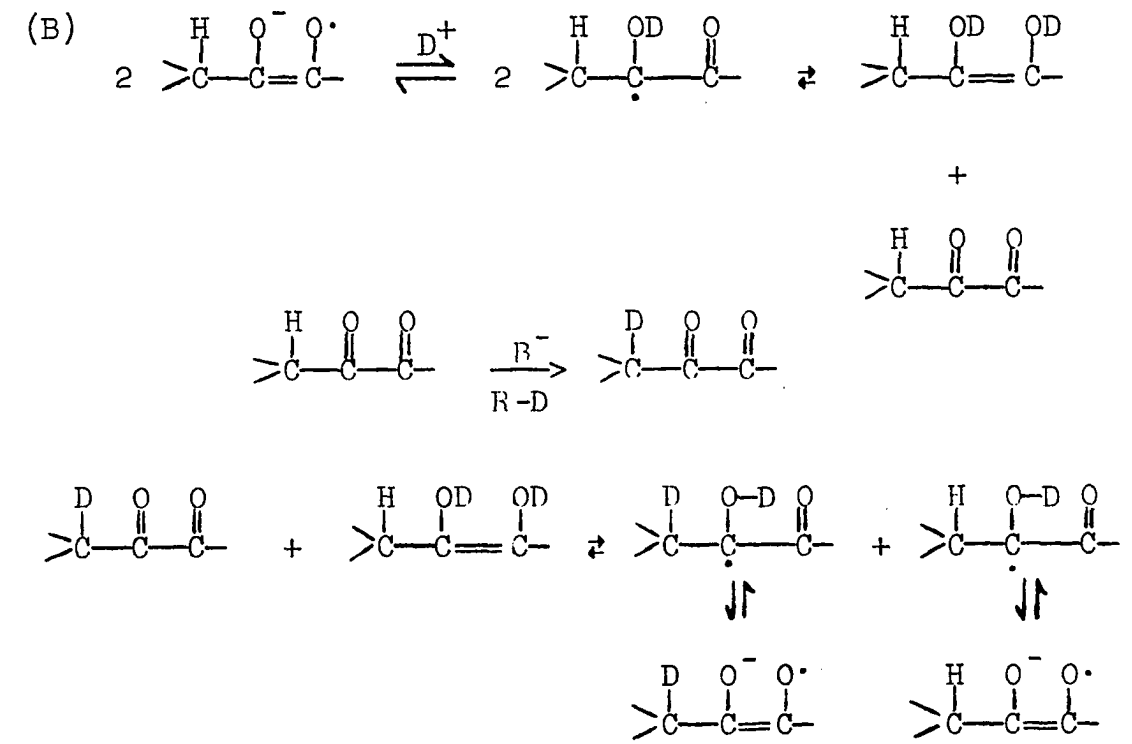
Chart XII

(A)

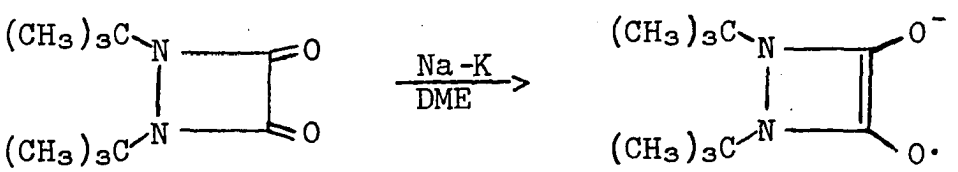


[a]This may be a general trend. For example, when anti-6-ethylbicyclo[3.1.0]hexane-2,3-semidione is generated in dry d_6-DMSO, only one of the α-hydrogens is exchanged within 18 hours (38) whereas in the presence of 2% deuterium oxide, both α-hydrogens are completely exchanged within 1 hour.

Chart XII continued

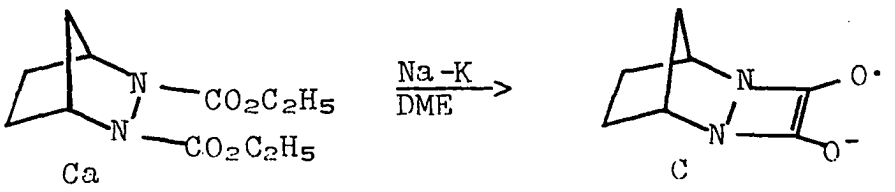


We did a very brief study of cyclobutanesemidiones containing heteroatoms. When di-t-butyl-1,2-diazetidinedione XCIXa (55) was reduced with sodium-potassium alloy in DME, an ESR spectrum (Figure 82; a^N = 1.68 (2N) gauss) was obtained which was assigned to XCIX.



XCIXa XCIX

Reactions of the type,



Ca C

were unsuccessful. The diketones in these bicyclic systems were not sufficiently stable at room temperature for our studies. We also enjoyed little success in the preparation of semidiones CI and CII (see section on Rearrangements Under Acyloin Conditions in the Appendix for a discussion of CII).

CI CII

ESR SPECTRA

Figure 1. First derivative ESR spectrum of bicyclo[4.2.0]octane-7,8-semidione (XCI) prepared by the *in situ* acyloin condensation of 0.2 M diethyl *cis*-cyclohexane-1,2-dicarboxylate with sodium-potassium alloy in DME.

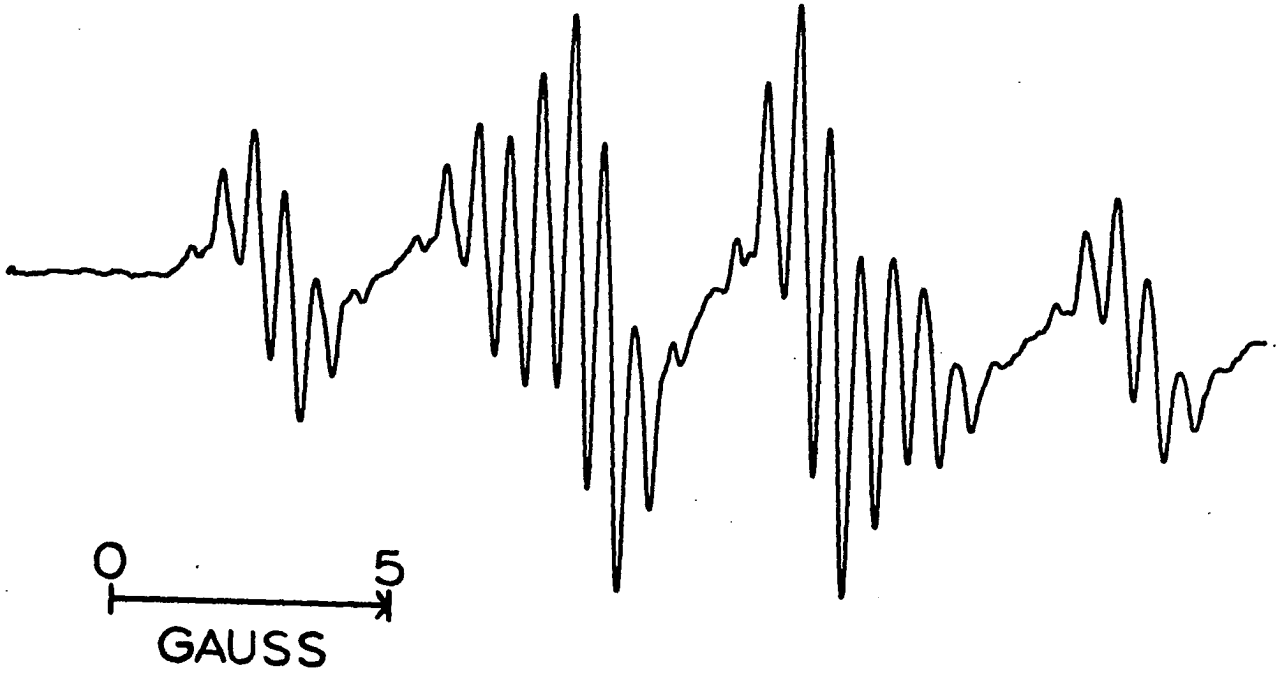


Figure 2. First derivative ESR spectrum of bicyclo[3.2.1]octane-6,7-semidione prepared by the <u>in situ</u> acyloin condensation of 0.2 M diethyl <u>cis</u>-cyclohexane-1,3-dicarboxylate with sodium-potassium alloy in DME.

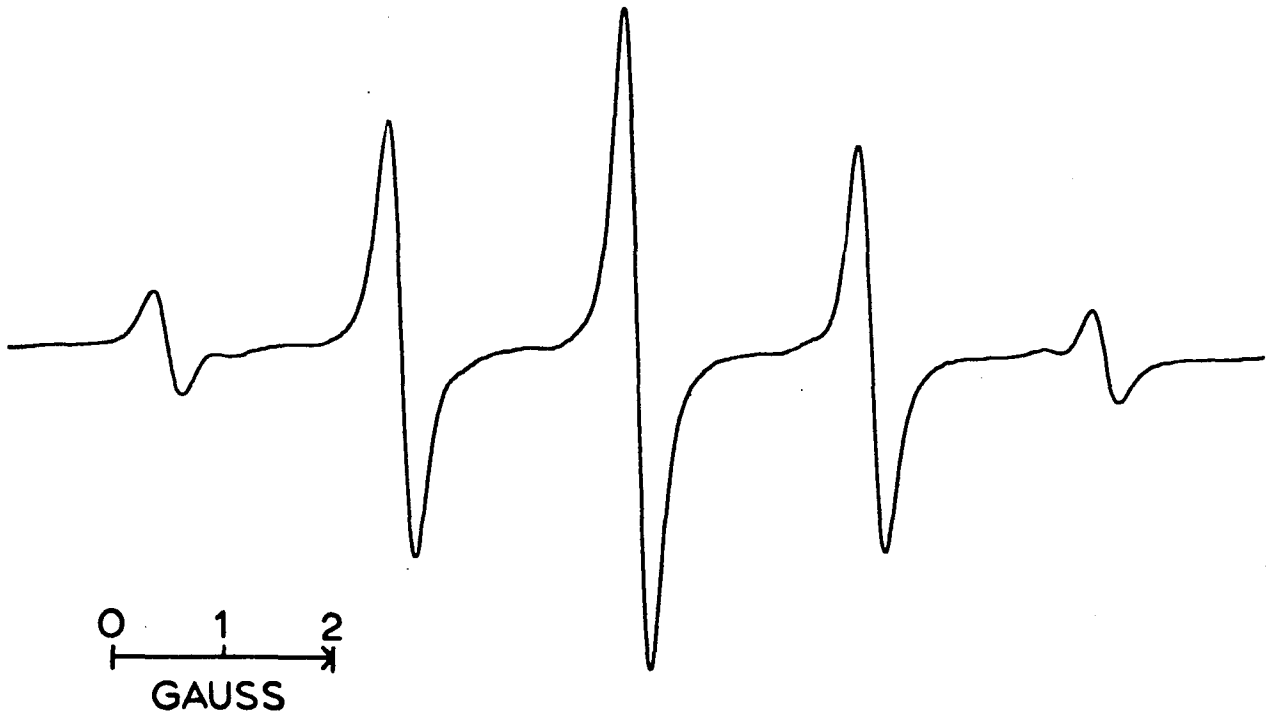


Figure 3. First derivative ESR spectrum of bicyclo[2.2.2]octane-2,3-semidione prepared by the <u>in situ</u> acyloin condensation of 0.2 M diethyl <u>cis</u>-cyclohexane-1,4-dicarboxylate with sodium-potassium alloy in DME.

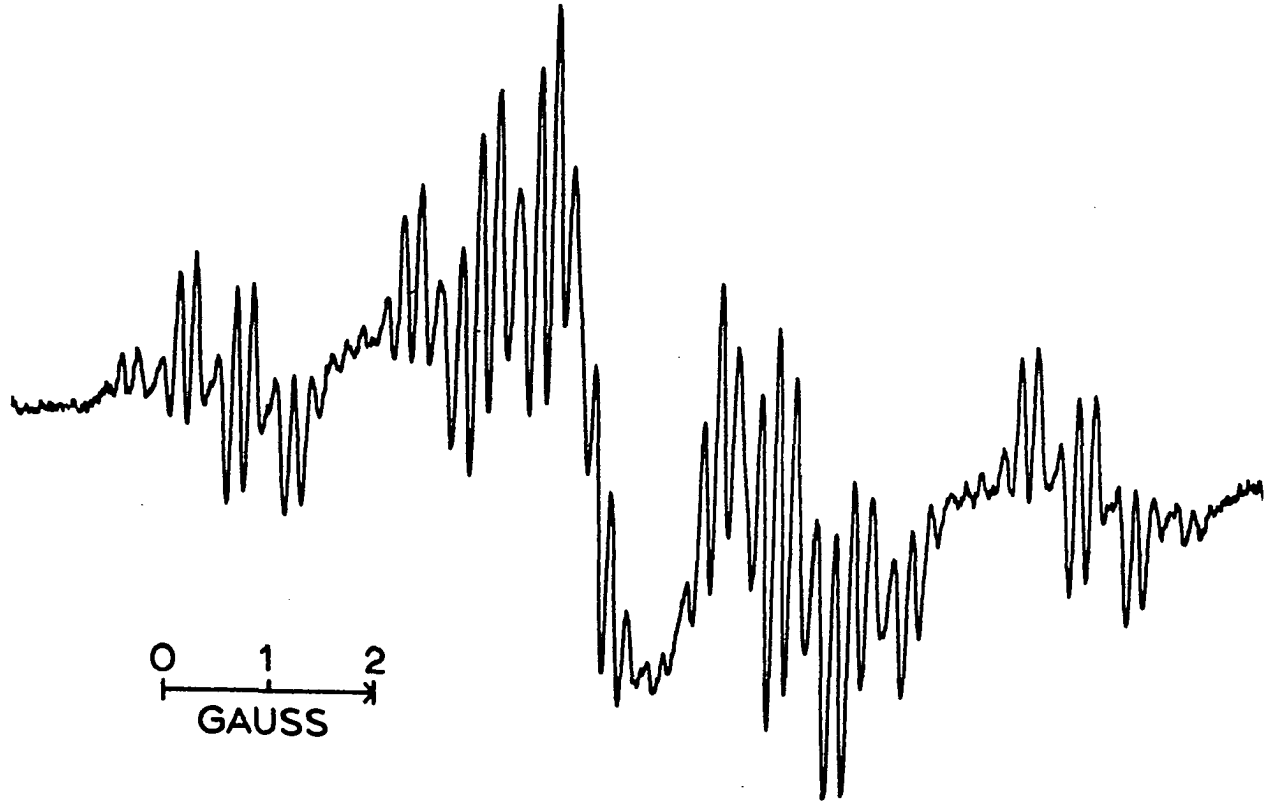


Figure 4. First derivative ESR spectrum of 1,7,7-trimethylbicyclo[2.2.1]heptane-2,3-semidione prepared by the acyloin condensation of 0.2 M dimethyl 1,2,2-trimethyl-cis-cyclopentane-1,3-dicarboxylate with sodium-potassium alloy in DME, followed by reaction of a filtered aliquot with an equal volume of 0.1 M potassium t-butoxide in DMSO.

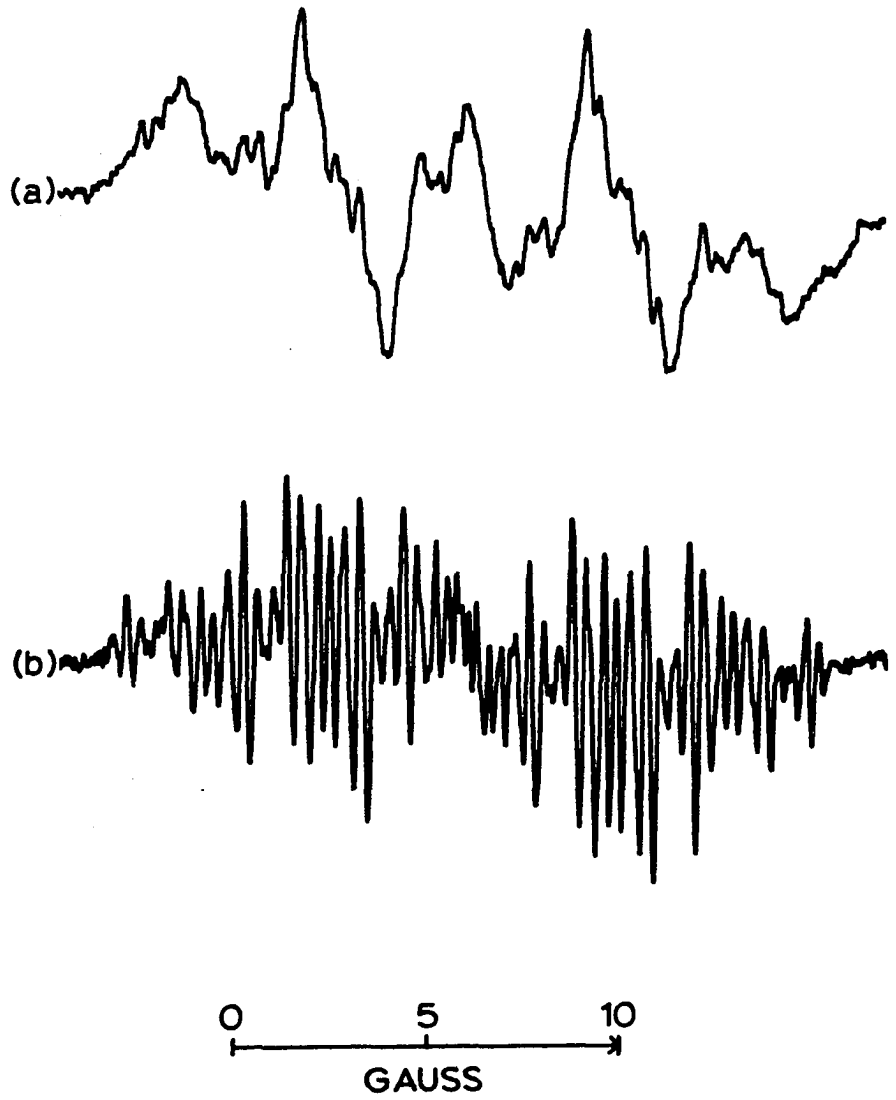


Figure 5. First derivative ESR spectrum of octahydro-exo-1,4-endo-5,8-dimethanonaphthalene-2,3-semidione prepared by: (a) the in situ acyloin condensation of 0.2 M dimethyl octahydro-exo-4,7-methanoindene-cis-1,3-dicarboxylate (β-isomer) with sodium-potassium alloy in DME, and (b) reaction of a filtered aliquot of the above solution with an equal volume of 0.1 M potassium t-butoxide in DMSO.

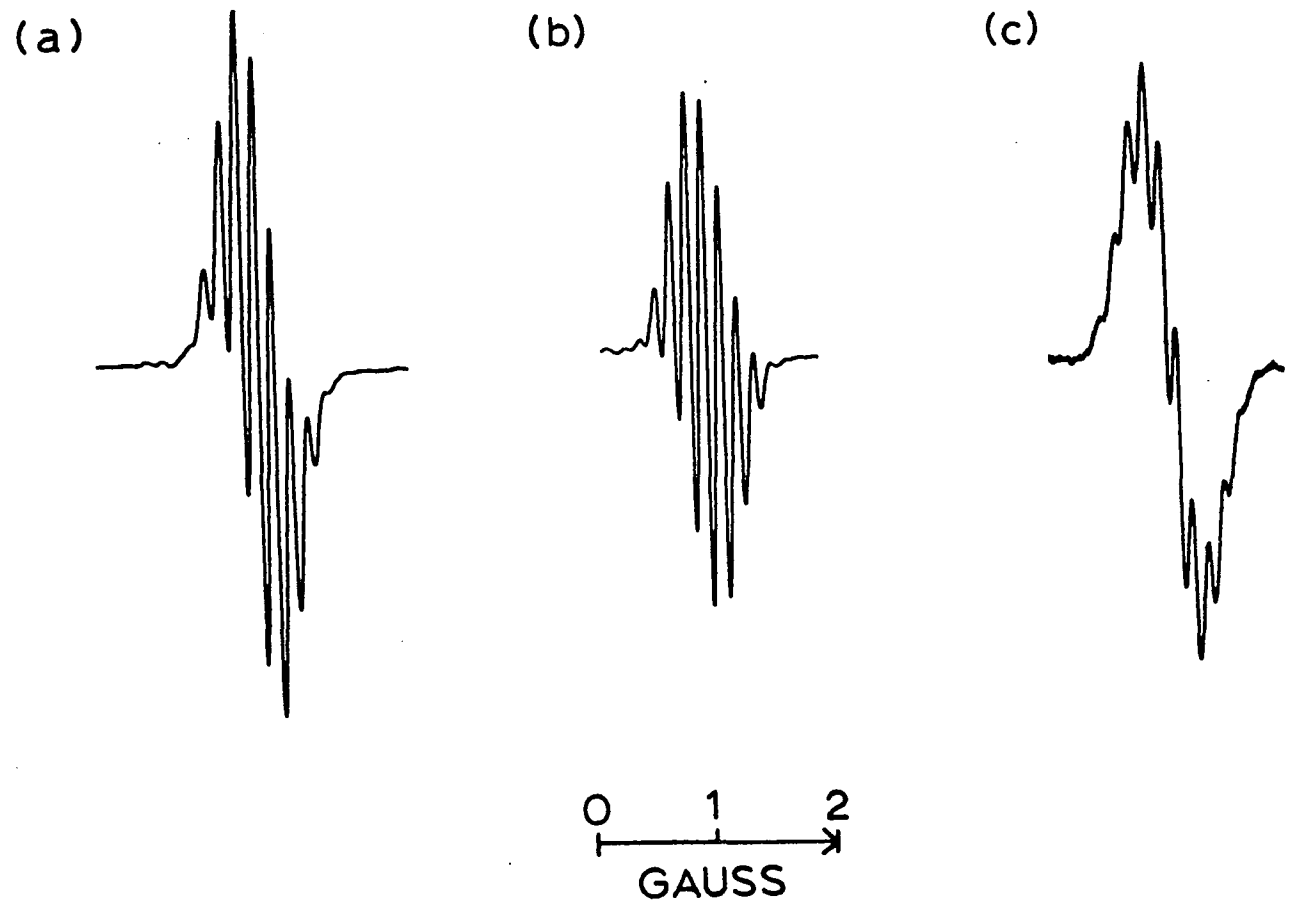


Figure 6. First derivative ESR spectra of (a) 5,6; 7,8-dibenzobicyclo[2.2.2] octa-5,7-diene-2,3-semidione, (b) 1,4-dideuterio-5,6; 7,8-dibenzobicyclo[2.2.2]-octa-5,7-diene-2,3-semidione, and (c) 1-methyl-5,6; 7,8-dibenzobicyclo-[2.2.2]octa-5,7-diene-2,3-semidione, prepared by the reaction of the corresponding crude bis(trimethylsiloxy)alkenes with potassium t-butoxide in DMSO.

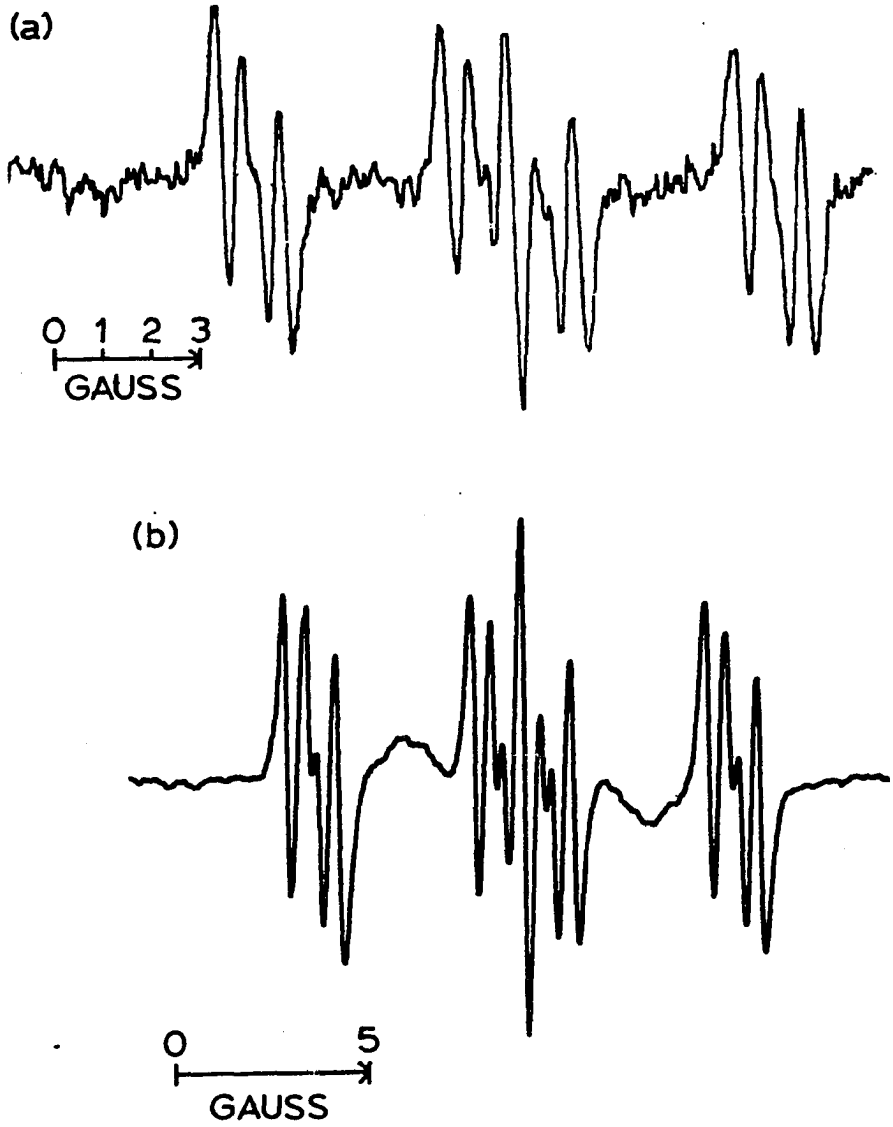


Figure 7. First derivative ESR spectra of 1-isopropyl-4-methylbicyclo[3.1.0]hexane-2,3-semidione (V) prepared by (a) the oxidation of thujone (0.2M) with potassium t-butoxide (0.4M) in DMSO and (b) the acyloin condensation of dimethyl homothujadicarboxylate (0.2M) with sodium-potassium alloy in DME, followed by reaction of a filtered aliquot with an equal volume of 0.1 M potassium t-butoxide in DMSO.

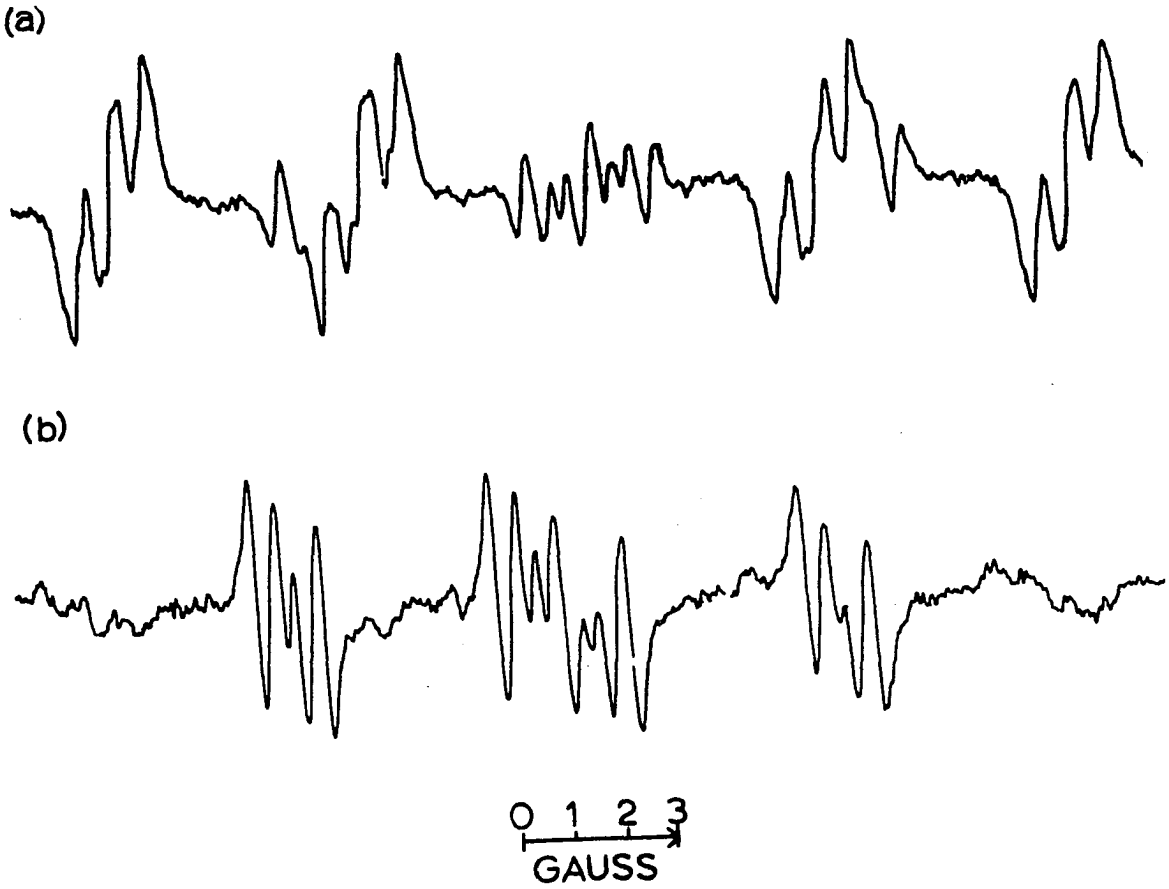


Figure 8. First derivative ESR spectra of the epimeric 1-isopropyl-4-methyl-bicyclo[3.1.0]hexane-2,3-semidiones (V and VI) prepared by the oxidation of β-dihydroumbellulone (0.1M) in DMSO containing potassium t-butoxide (0.3M); (a) reaction time 20 minutes and (b) reaction time 360 minutes.

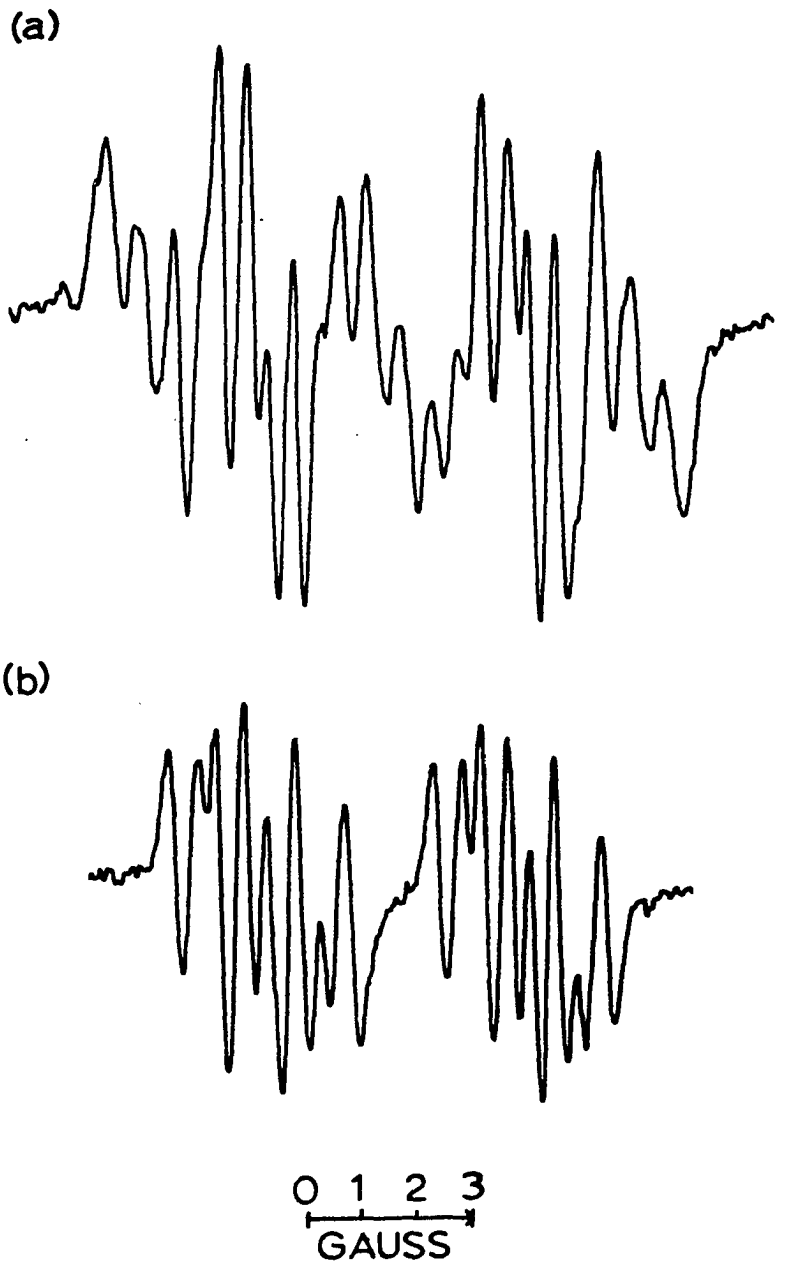


Figure 9. First derivative ESR spectra of the epimeric 1-isopropyl-4-deuterio-4-methylbicyclo[3.1.0]hexane-2,3-semidiones prepared by the oxidation of (a) β-dihydroumbellulone (0.1M) (reaction time 50 minutes) and (b) thujone (0.1M) in d_6-DMSO containing potassium t-butoxide (0.3M).

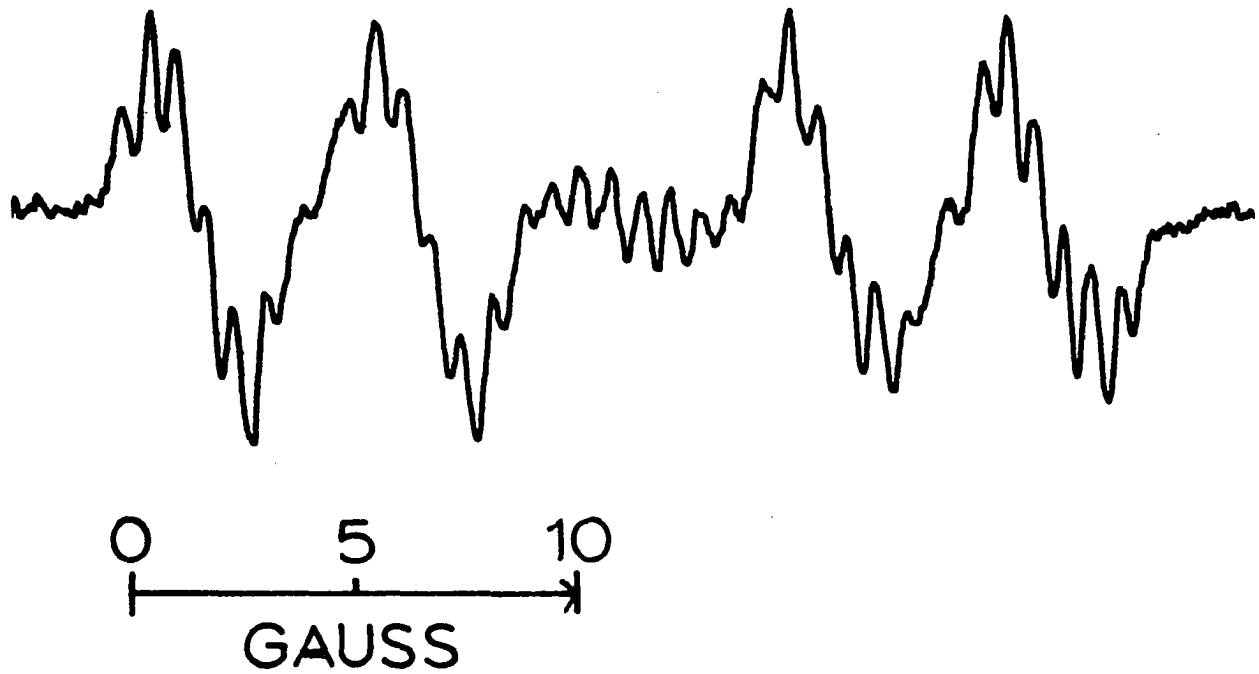


Figure 10. First derivative ESR spectrum of 1-isopropyl-4-endo-methylbicyclo-[3.1.0]hexane-2,3-semidione (VI) prepared by the oxidation of β-dihydroumbellulone (0.1M) in DMSO containing sodium t-butoxide (0.2M).

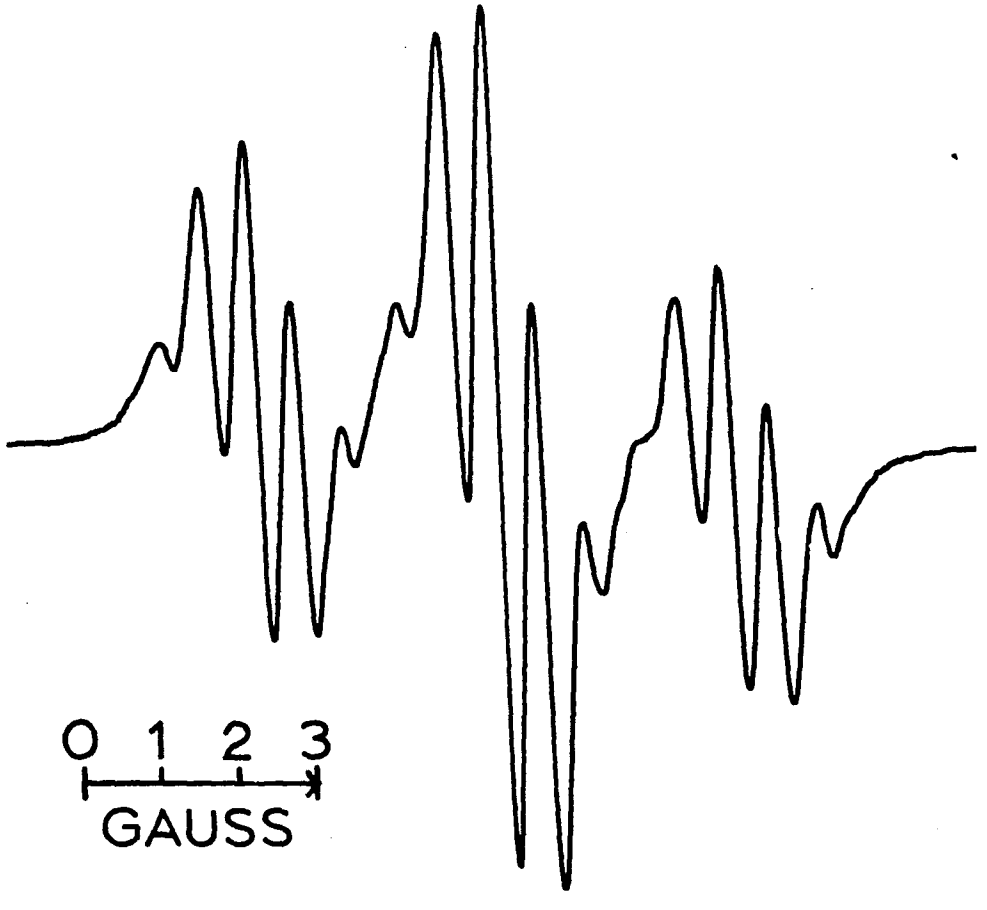


Figure 11. First derivative ESR spectrum of 3-methyl-5-isopropyl-o-benzosemiquinone (VII) prepared by the overoxidation of β-dihydroumbellulone (0.1 M) in DMSO:t-BuOH (90:10) containing potassium t-butoxide (0.3 M).

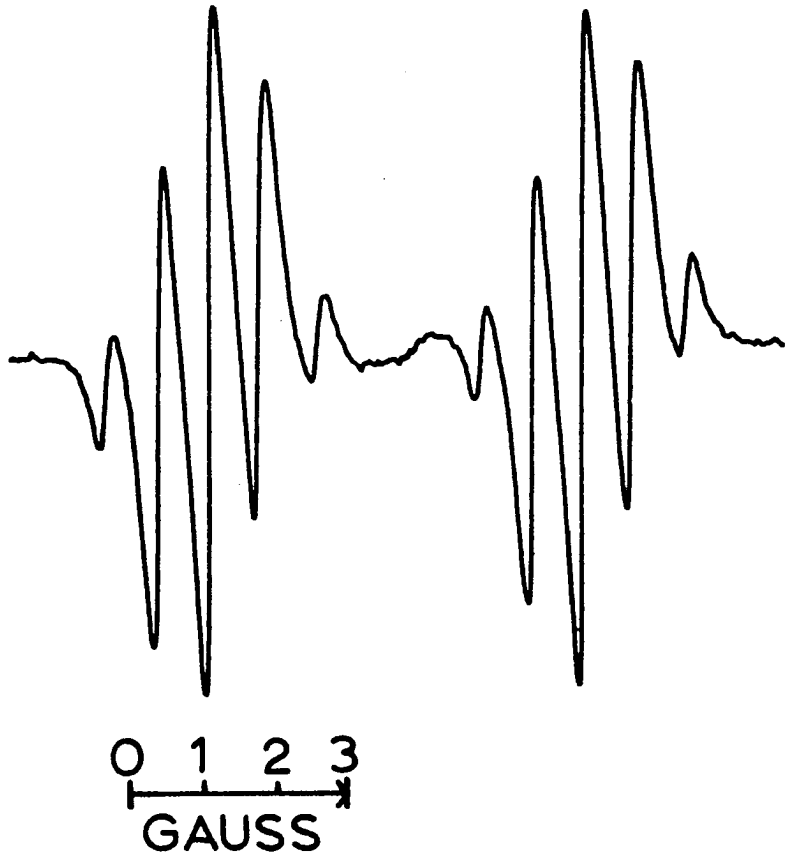


Figure 12. First derivative ESR spectrum of 3-methyl-4-oxy-6-isopropyl-o-benzosemiquinone (IX) prepared by the overoxidation of 2,3-dihydroxycymene (0.1 M) in DMSO containing potassium t-butoxide (0.3 M).

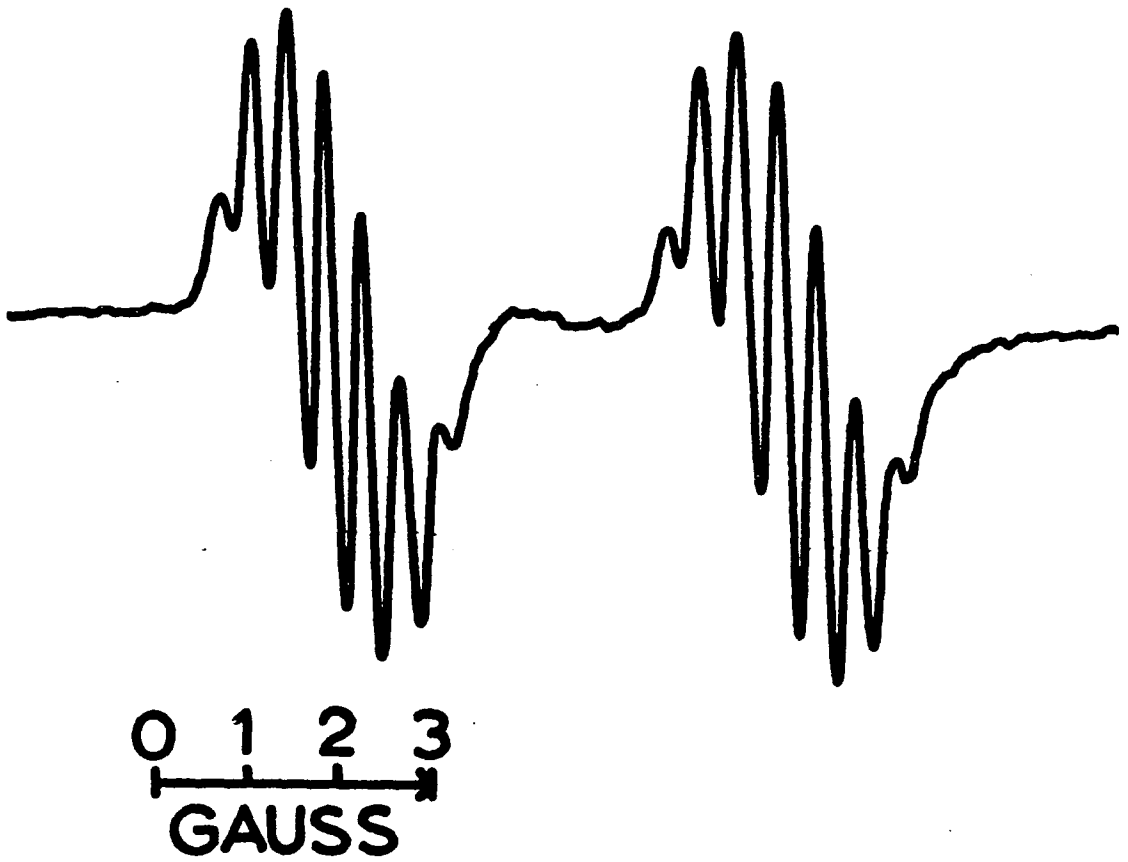


Figure 13. First derivative ESR spectrum of 1-isopropyl-4,4-dimethylbicyclo[3.1.0]-hexane-2,3-semidione (XII) prepared by the reaction of 0.1 M 2-n-butyl-thiomethylene-4,4-dimethyl-1-isopropylbicyclo[3.1.0]hexan-3-one with 0.3 M potassium t-butoxide and air in DMSO.

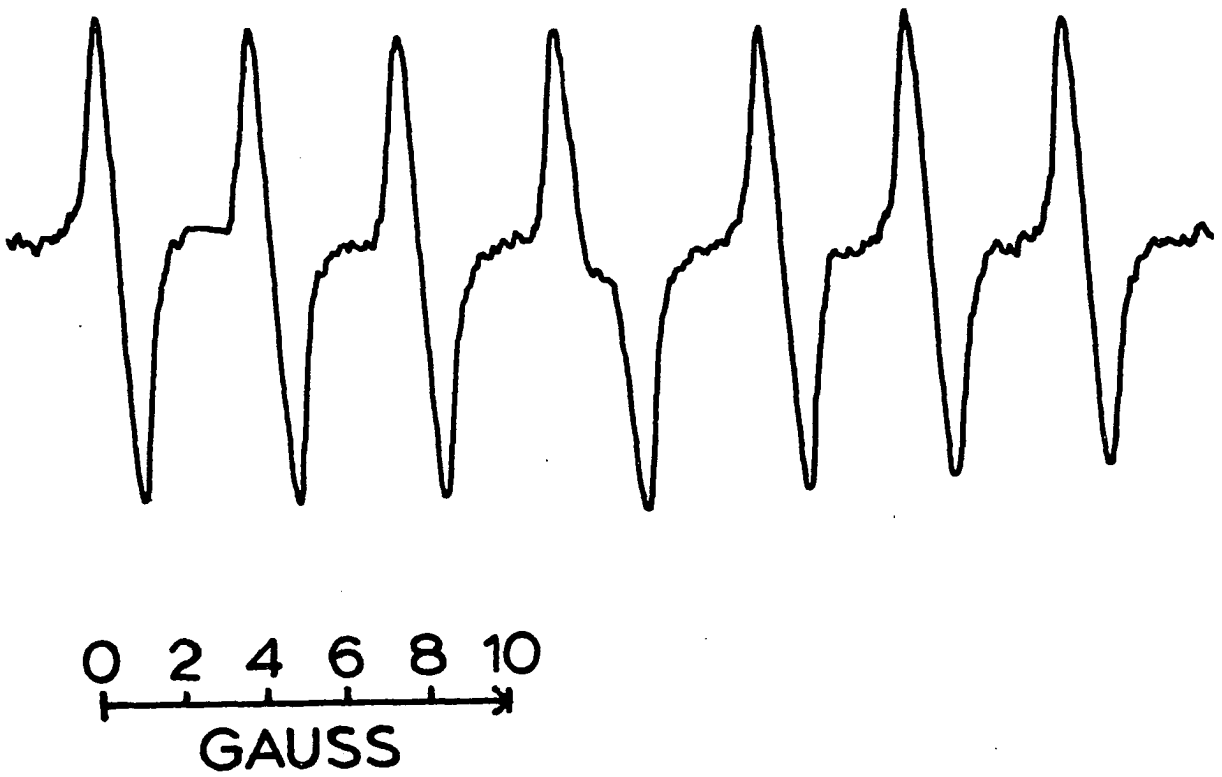


Figure 14. First derivative ESR spectrum of the semidione generated by the reaction of cis-10β-methyl-7α-isopropyl-2-n-butylthiomethylene-1-decalone with air and potassium t-butoxide in DMSO.

Figure 15. First derivative ESR spectrum of 5-isopropylbicyclo[3.1.0]hexane-2,3-semidione (XIII) prepared by the oxidation of sabina ketone (0.1 M) in DMSO containing potassium t-butoxide (0.3 M).

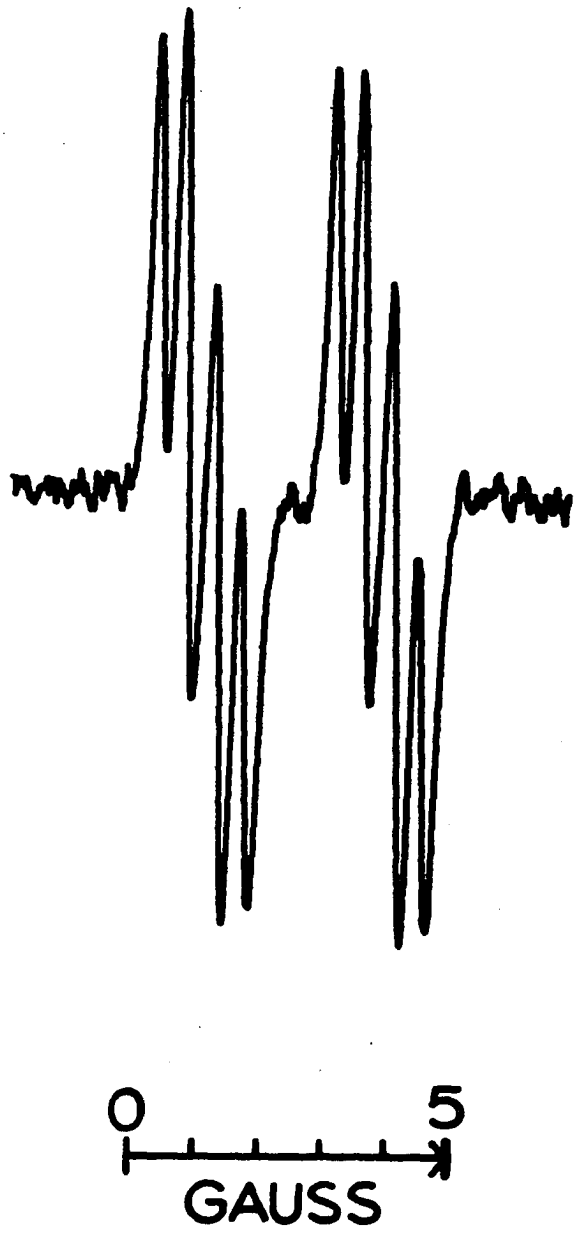


Figure 16. First derivative ESR spectrum of the secondary radical anion which is produced from 5-isopropyl-bicyclo[3.1.0]hexane-2,3-semidione in d_6-DMSO containing potassium t-butoxide (recorded 4 hours after initial oxidation of sabina ketone).

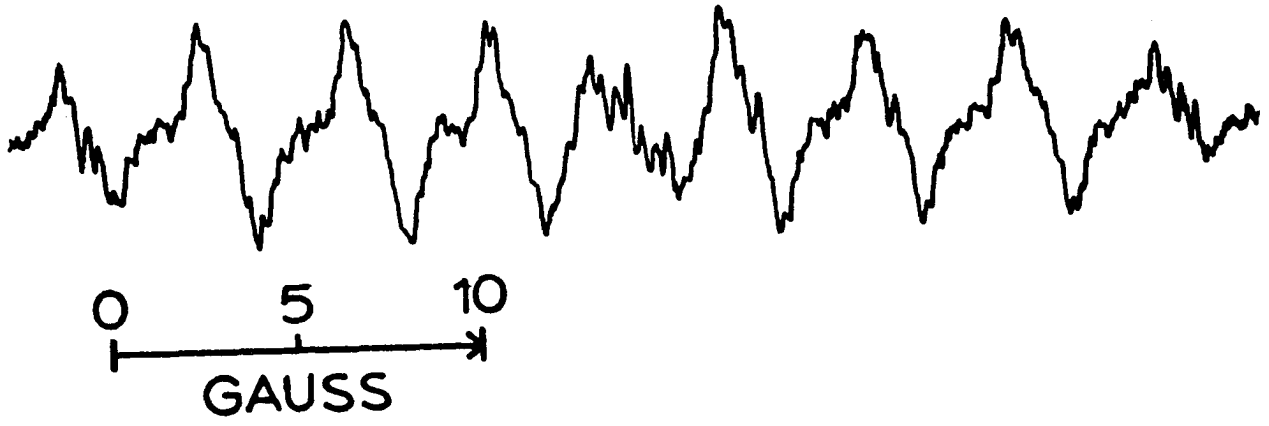


Figure 17. First derivative ESR spectrum of 5-methylbicyclo[3.1.0]hexane-2,3-semidione (XV) prepared by the oxidation of 5-methylbicyclo[3.1.0]-hexan-2-one (0.2 M) in DMSO containing cesium t-butoxide (0.4 M).

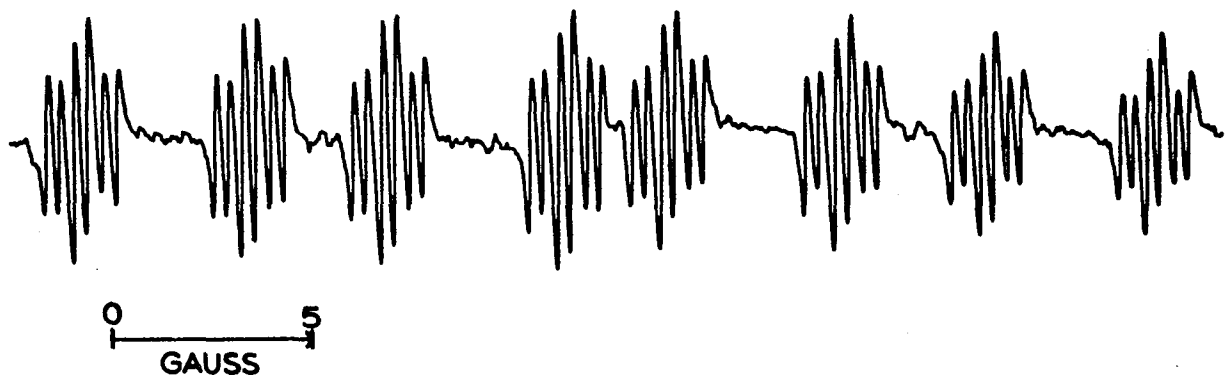


Figure 18. First derivative ESR spectrum of anti-6-(methoxymethyl)bicyclo[3.1.0]-hexane-2,3-semidione (XVII) prepared by the oxidation of syn-6-(methoxy-methyl)bicyclo[3.1.0]hexan-3-one (0.1 M) in DMSO containing potassium t-butoxide (0.2 M) (spectrum recorded 5 hours after initial oxidation was begun).

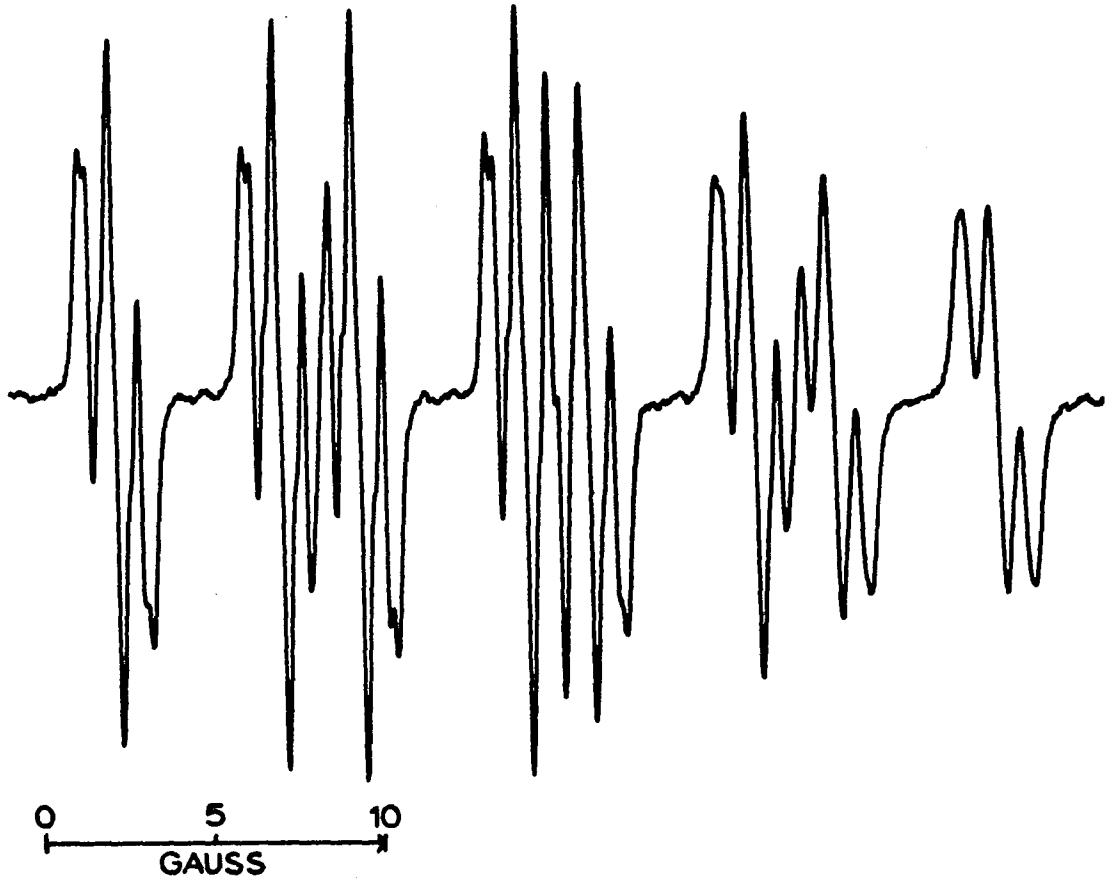


Figure 19. First derivative ESR spectrum of the semidione XIX derived from the oxidation of syn-bicyclo[3.1.0]hexan-2-one-6-spiro-1'-(2',2'-dimethylcyclopentane) (0.1 M) in DMSO containing potassium t-butoxide (0.2 M).

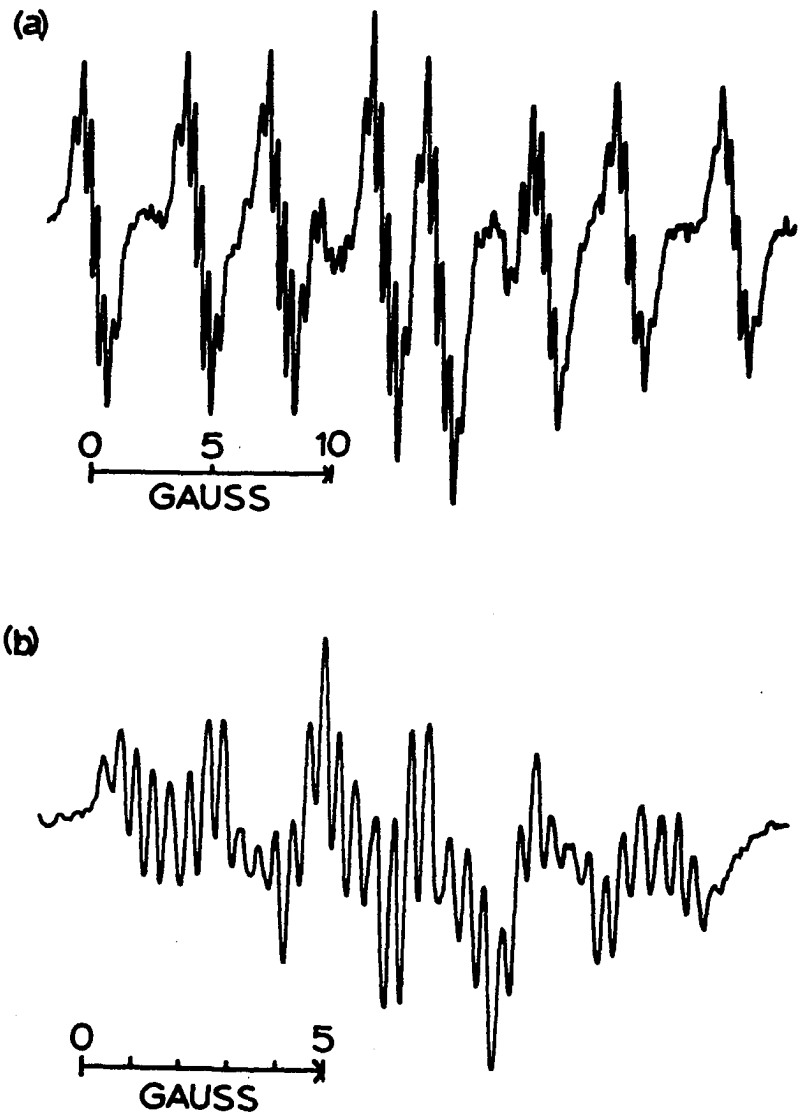


Figure 20. First derivative ESR spectra of tricyclo-[4.3.1.$0^{1,6}$]decane-7,8-semidione (XXII) prepared by the oxidation of tricyclo[4.3.1.$0^{1,6}$]decan-7-one (0.1 M) in d_6-DMSO containing potassium t-butoxide (0.3 M); (a) spectrum recorded after 10 minutes; (b) spectrum recorded after 2 hours.

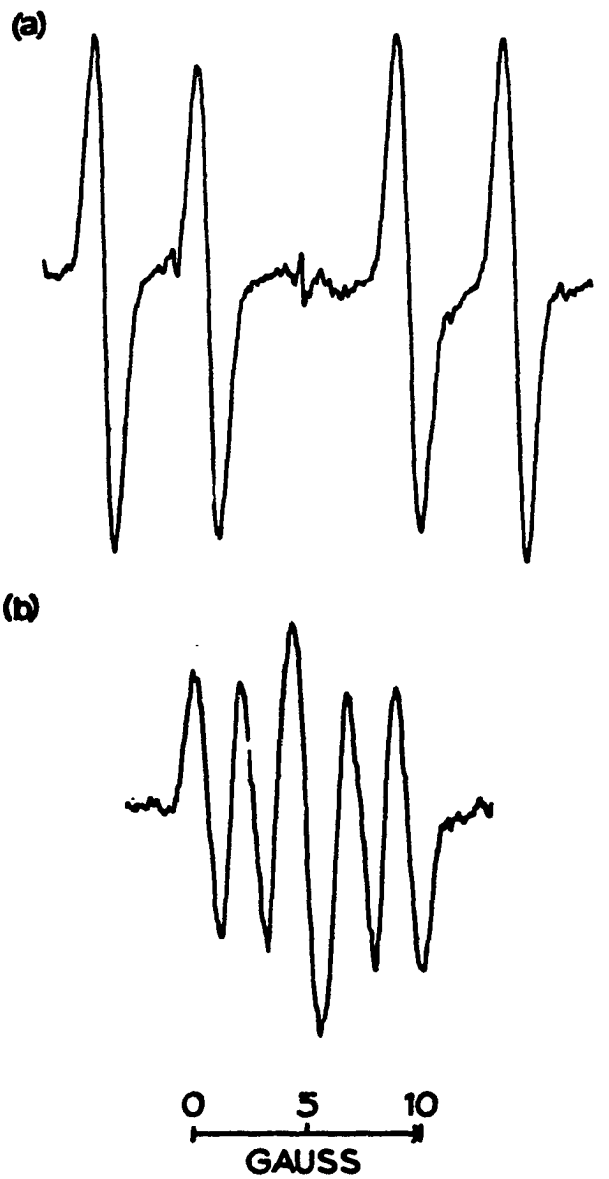


Figure 21. First derivative ESR spectra of (a) 9-methyltricyclo[4.3.1.$0^{1,6}$]decane-7,8-semidione (XXIII) prepared by the oxidation of 9-methyltricyclo-[4.3.1.$0^{1,6}$]decan-7-one (0.2 M) in DMSO containing potassium t-butoxide (0.4 M), and (b) 9-deuterio-9-methyltricyclo[4.3.1.$0^{1,6}$]decan-7,8-semidione prepared by the oxidation of 9-methyltricyclo-[4.3.1.$0^{1,6}$]decan-7-one (0.1 M) in d_6-DMSO containing potassium t-butoxide (0.3 M).

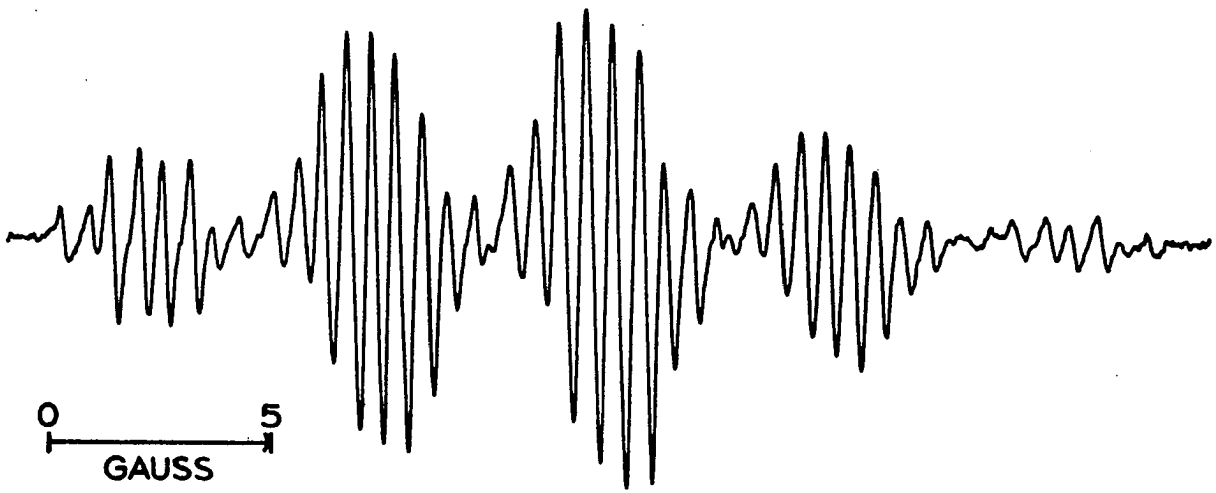


Figure 22. First derivative ESR spectrum of the secondary radical derived from 9-methyltricyclo[4.3.1.$0^{1,6}$]decane-7,8-semidione, prepared by admitting excess oxygen to a solution of 9-methyltricyclo[4.3.1.$0^{1,6}$]-decan-7-one (0.1 M) in DMSO containing potassium t-butoxide (0.2 M).

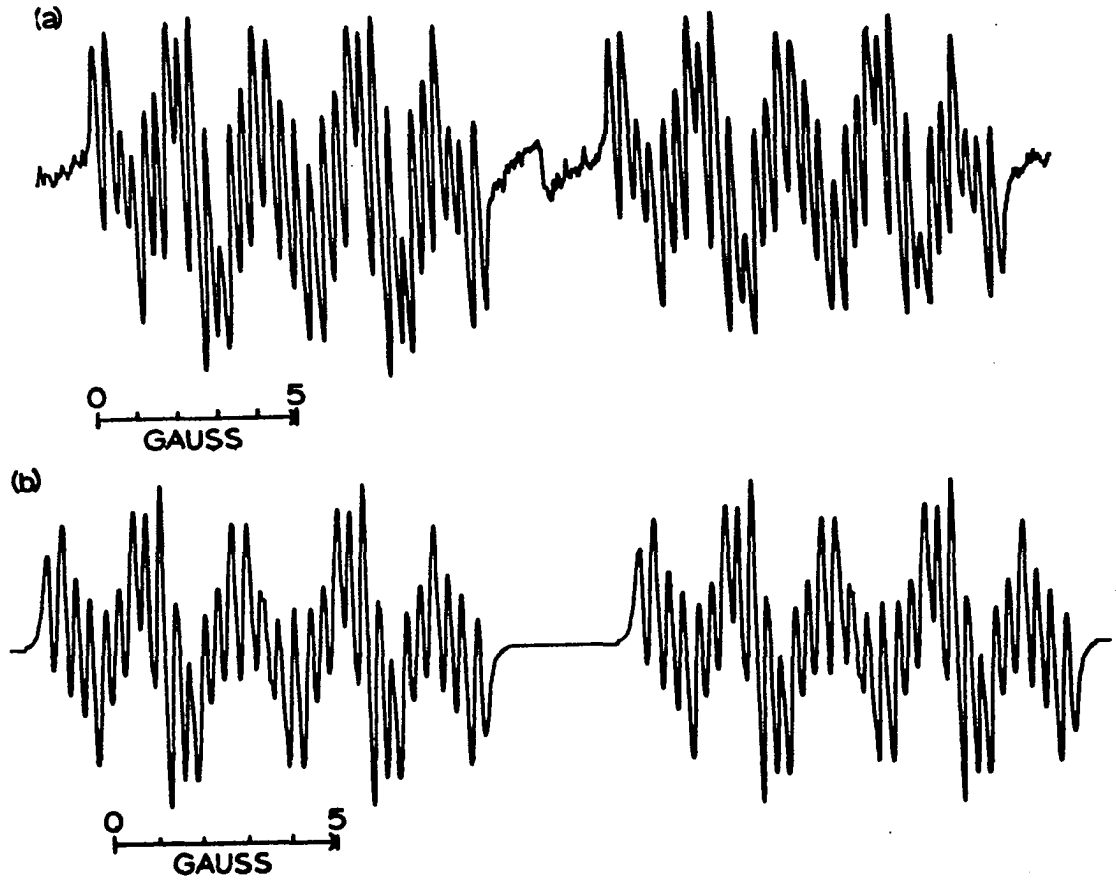


Figure 23. (a) First derivative ESR spectrum of bicyclo[4.1.0]heptane-2,3-semidione (XXV) prepared by the oxidation of bicyclo[4.1.0]heptan-2-one (0.2 M) in DMSO containing potassium t-butoxide (0.4 M); (b) Simulated spectrum for Lorentzian linewidth of 0.30 gauss and hfsc from text performed by JEOLCO JNM-RA-1 spectrum accumulator.

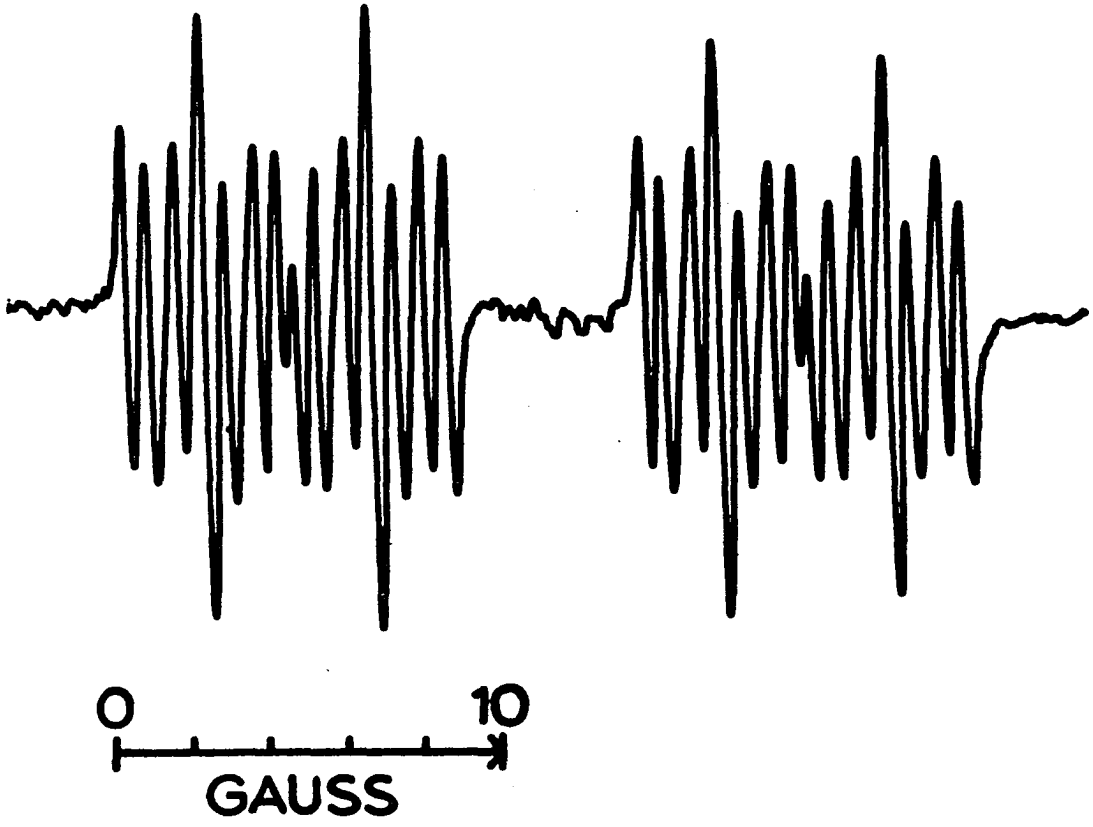


Figure 24. First derivative ESR spectrum of 5,5-dimethylbicyclo[4.1.0]heptane-2,3-semidione (XXVI) prepared by the reduction of 5,5-dimethylbicyclo-[4.1.0]heptan-2,3-dione (0.05 M) in DMSO containing propiophenone (0.02 M) and potassium t-butoxide (0.1 M).

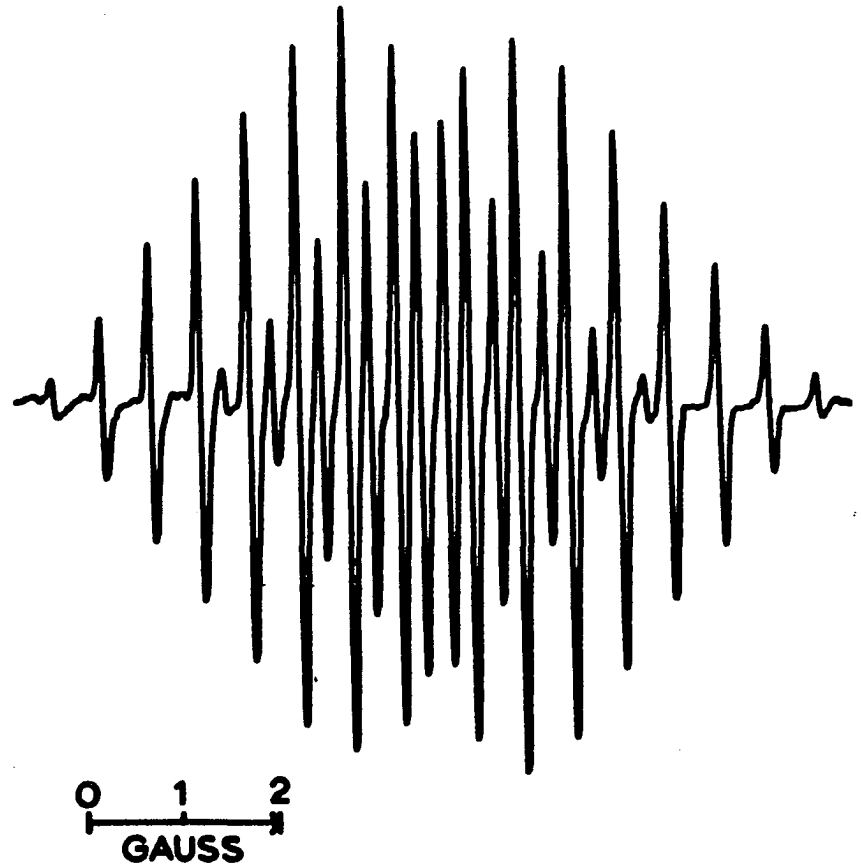


Figure 25. First derivative ESR spectrum of 4,4-dideutero-5,5-dimethylbicyclo-[4.1.0]heptane-2,3-semidione prepared by the reduction of 5,5-dimethyl-bicyclo[4.1.0]heptan-2,3-dione (0.05 M) in d_6-DMSO containing propio-phenone (0.02 M) and potassium t-butoxide (0.1 M).

Figure 26. First derivative ESR spectrum of 1-methylbicyclo[4.1.0]heptane-2,3-semidione (XXVII) prepared by the oxidation of 1-methylbicyclo[4.1.0]-heptan-2-one (0.2 M) in DMSO containing potassium t-butoxide (0.4 M).

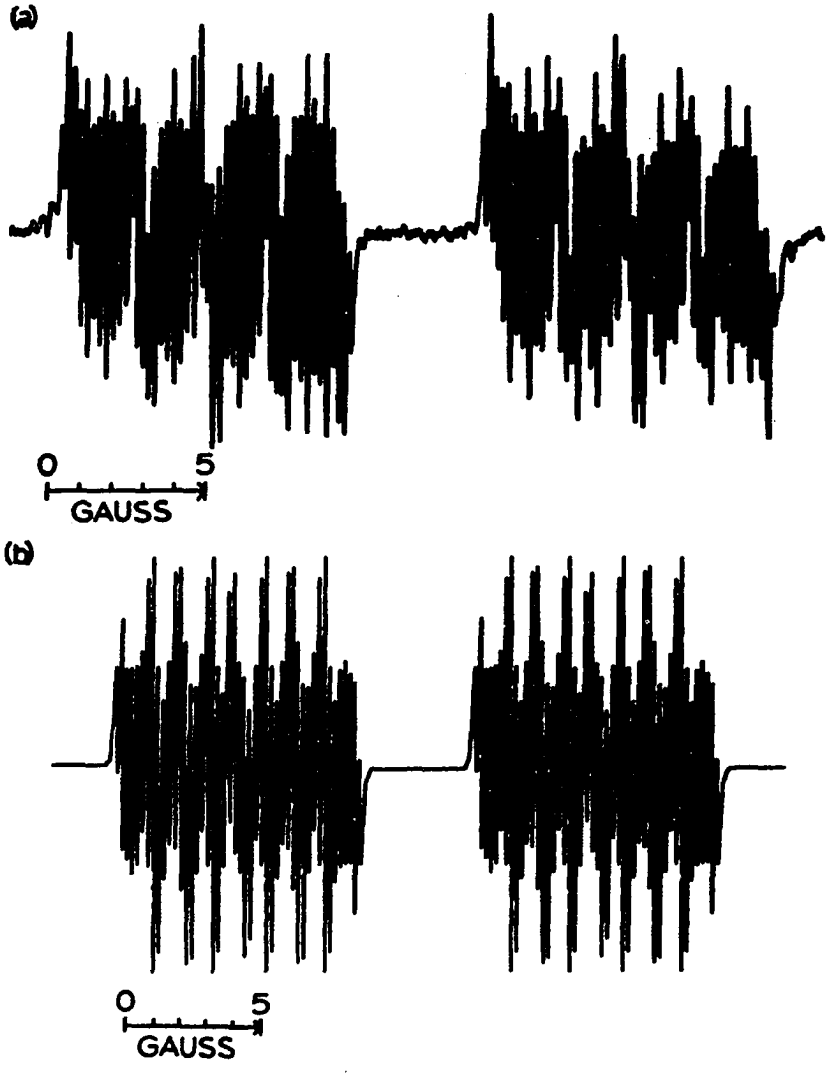


Figure 27. (a) First derivative ESR spectrum of tricyclo-[5.4.0.$0^{1,3}$]undecane-4,5-semidione (XXVIII) prepared by the oxidation of tricyclo[5.4.0.$0^{1,3}$]-undecan-4-one (0.1 M) in DMSO containing potassium t-butoxide (0.3 M); (b) simulated spectrum for Lorentzian linewidth of 0.20 gauss and hfsc from text performed by JEOLCO JNM-RA-1 spectrum accumulator.

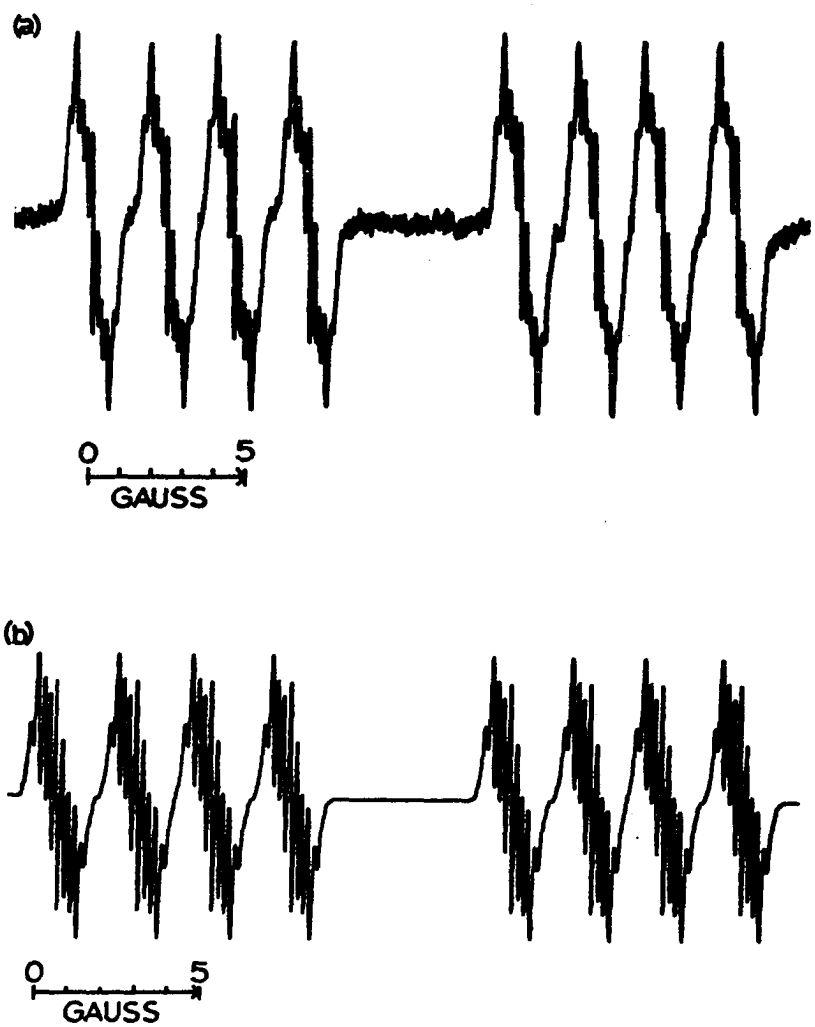


Figure 28. (a) First derivative ESR spectrum of 3-methyltricyclo[5.4.0.$0^{1,3}$]undecane-4,5-semidione (XXIX) prepared by the oxidation of 3-methyltricyclo-[5.4.0.$0^{1,3}$]undecan-4-one (0.1 M) in DMSO containing potassium t-butoxide (0.3 M); (b) simulated spectrum for Lorentzian linewidth of 0.25 gauss and hfsc from text performed by JEOLCO JNM-RA-1 spectrum accumulator.

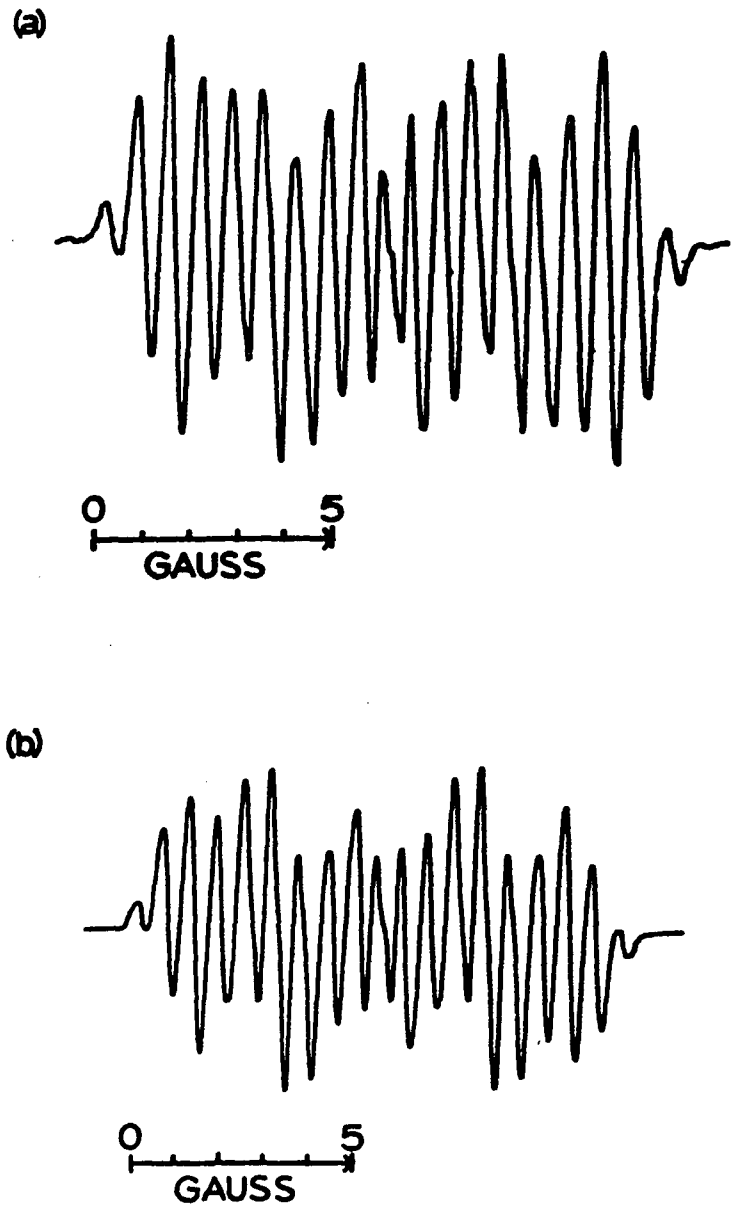


Figure 29. (a) First derivative ESR spectrum of 4,4,6-trimethylbicyclo[4.1.0]heptane-2,3-semidione (XXX) prepared by the oxidation of 4,4,6-trimethylbicyclo-[4.1.0]heptan-2-one (0.1 M) in DMSO containing potassium t-butoxide (0.5 M); (b) simulated spectrum for Lorentzian linewidth of 0.50 gauss and hfsc from text performed by JEOLCO JNM-RA-1 spectrum accumulator.

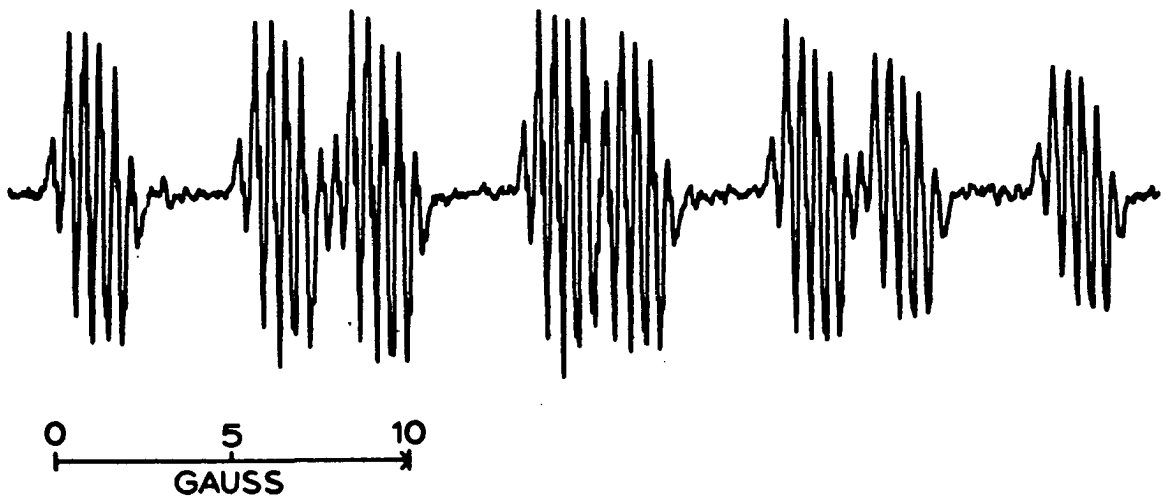


Figure 30. First derivative ESR spectrum of 7,7-dimethylbicyclo[4.1.0]heptane-2,3-semidione (XXXI) prepared by reacting the crude 7,7-dimethyl-2,3-bis(trimethylsiloxy)bicyclo[4.1.0]hept-2-ene (0.1 M) with potassium t-butoxide (0.2 M) in DMSO.

Figure 31. First derivative ESR spectra of the mixture of 4-deuterio- and 4,4-dideuterio-7,7-dimethyl-bicyclo[4.1.0]heptane-2,3-semidiones prepared by reacting the crude 7,7-dimethyl-2,3-bis(trimethylsiloxy)bicyclo[4.1.0]hept-2-ene (0.1 M) with potassium t-butoxide (0.2 M) in d_6-DMSO; (a) spectrum recorded after 1 hour; (b) spectrum recorded after 10 hours.

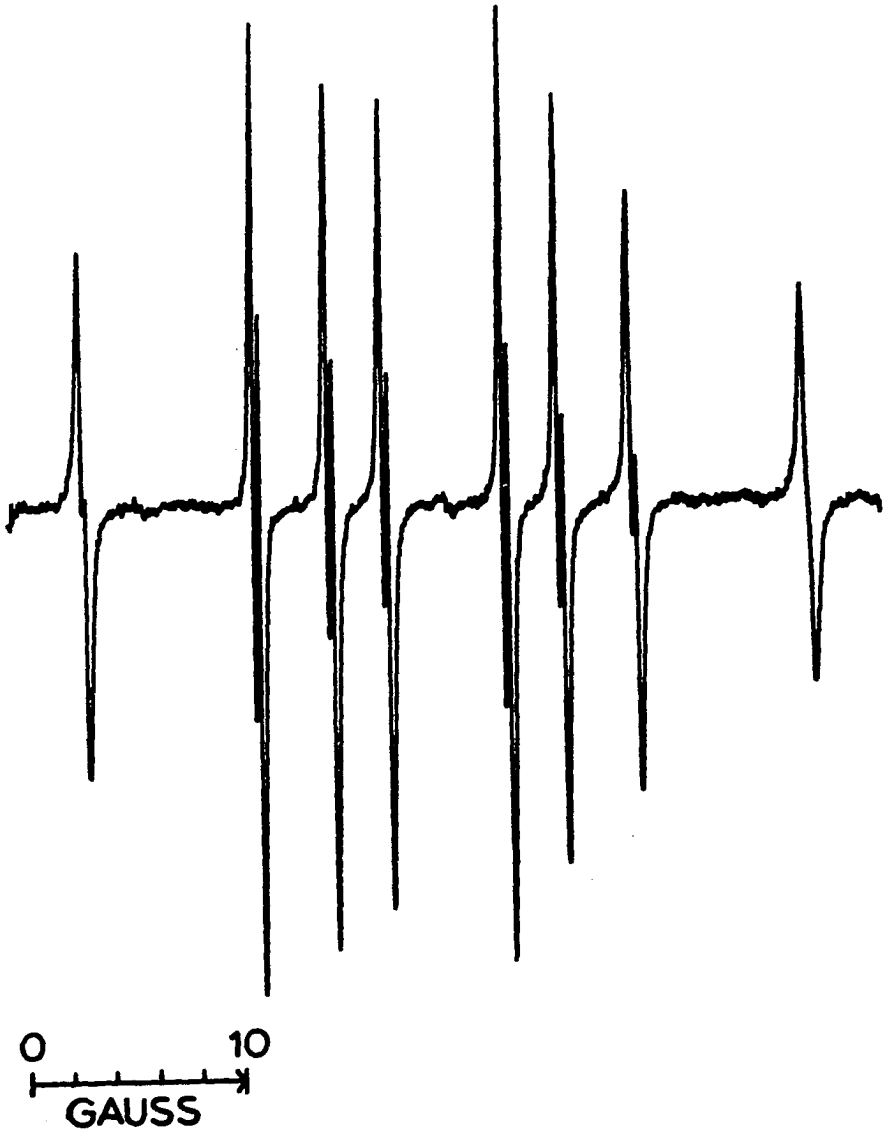


Figure 32. First derivative ESR spectrum of the semidione XXXVII prepared by the reaction of lumiisocolchicine ketol (0.05 M) with potassium t-butoxide (0.3 M) in DMSO.

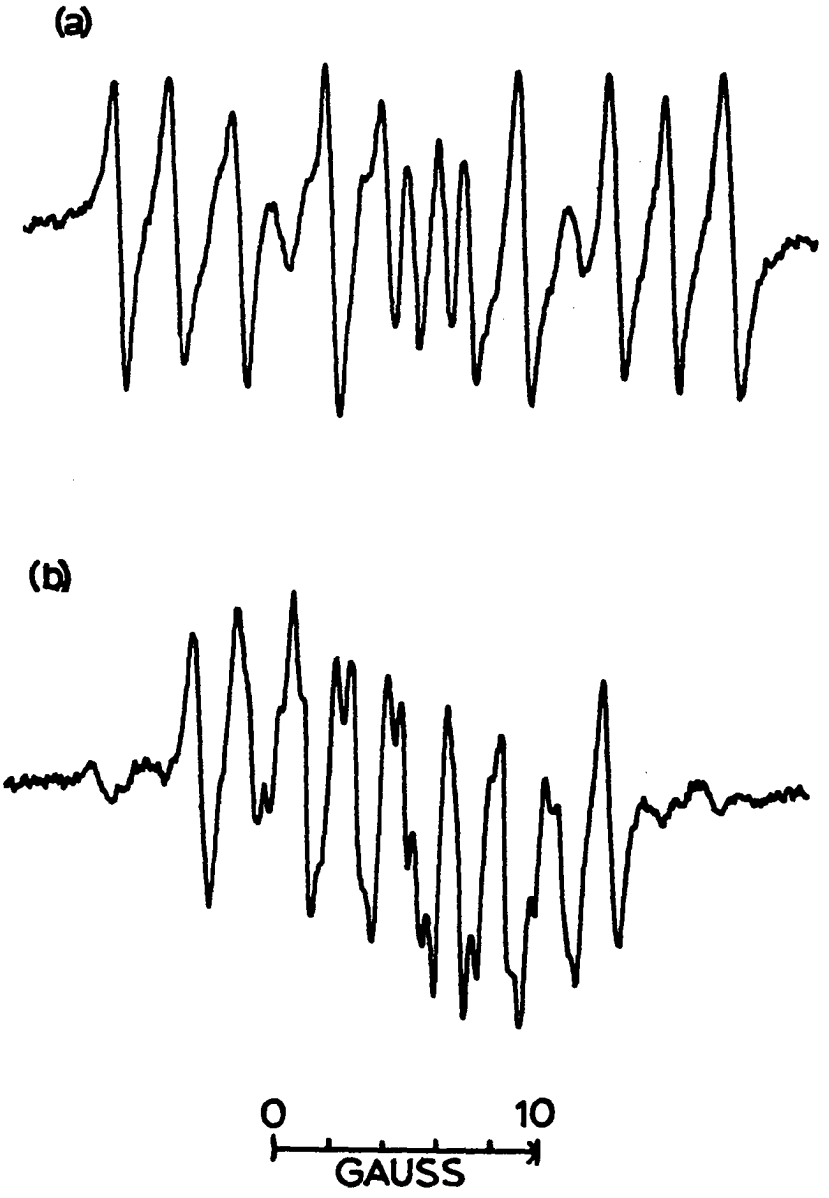


Figure 33. First derivative ESR spectra of the semidiones prepared by the reaction of lumiisocolchicine ketol (0.1 M) with potassium t-butoxide (0.3 M) in d_6-DMSO; (a) spectrum recorded after 1.5 hours; (b) spectrum recorded after 24 hours.

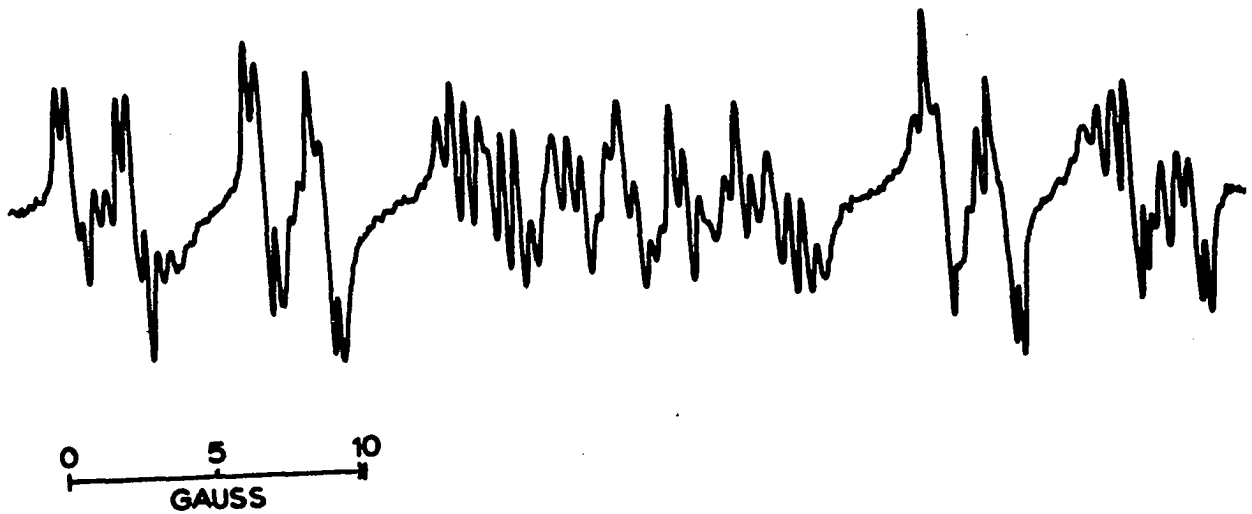


Figure 34. First derivative ESR spectrum of semidione XXXVIII prepared by the reaction of dihydrolumiisocolchicine ketol (0.05 M) with potassium t-butoxide (0.2 M) in DMSO.

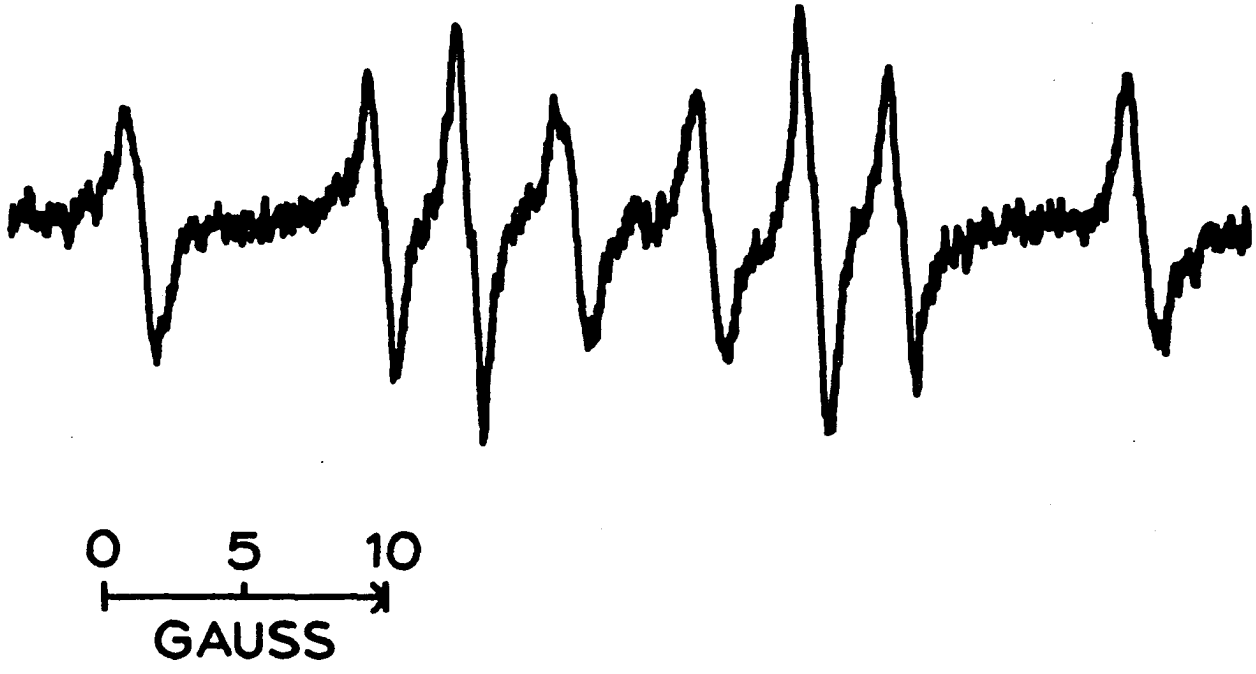


Figure 35. First derivative ESR spectrum of semidione XXXIX prepared by the reaction of β-lumicolchicine ketol (0.05 M) with potassium t-butoxide (0.2 M) in DMSO.

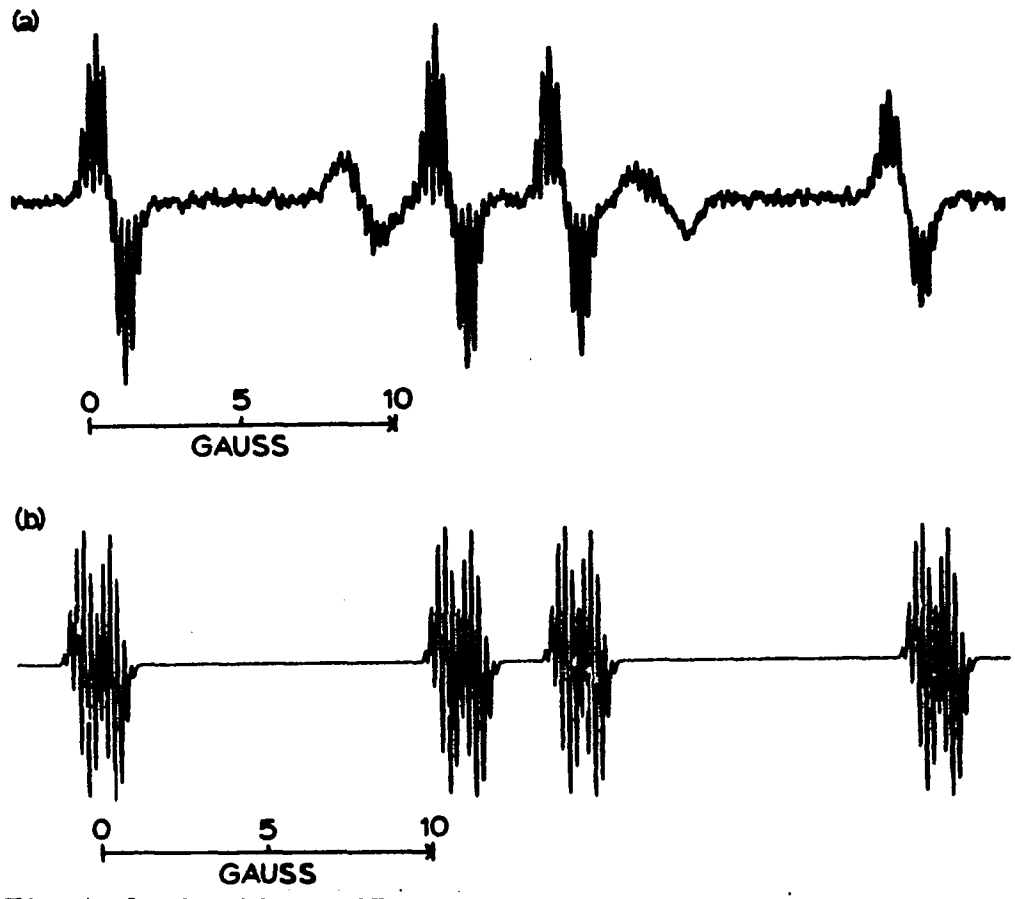


Figure 36. (a) First derivative ESR spectrum of 1,7-dimethylbicyclo[3.2.0]hept-6-ene-2,3-semidione (XL) prepared by the oxidation of 1,7-bicyclo[3.2.0]-hept-6-en-2-one (0.1 M) in DMSO containing potassium t-butoxide (0.3 M); (b) simulated spectrum for Lorentzian linewidth of 0.15 gauss and hfsc from text performed by JEOLCO JNM-RA-1 spectrum accumulator.

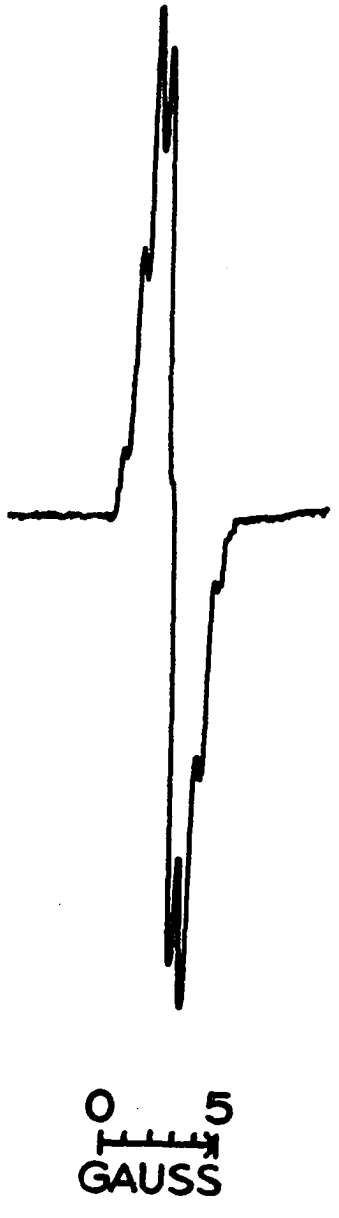


Figure 37. First derivative ESR spectrum of 1,4,4-trimethylbicyclo[3.2.0]heptane-2,3-semidione (XLI) prepared by the reduction of 1,4,4-trimethylbicyclo[3.2.0]heptan-2,3-dione (0.05 M) in DMSO containing propiophenone (0.02 M) and potassium t-butoxide (0.2 M).

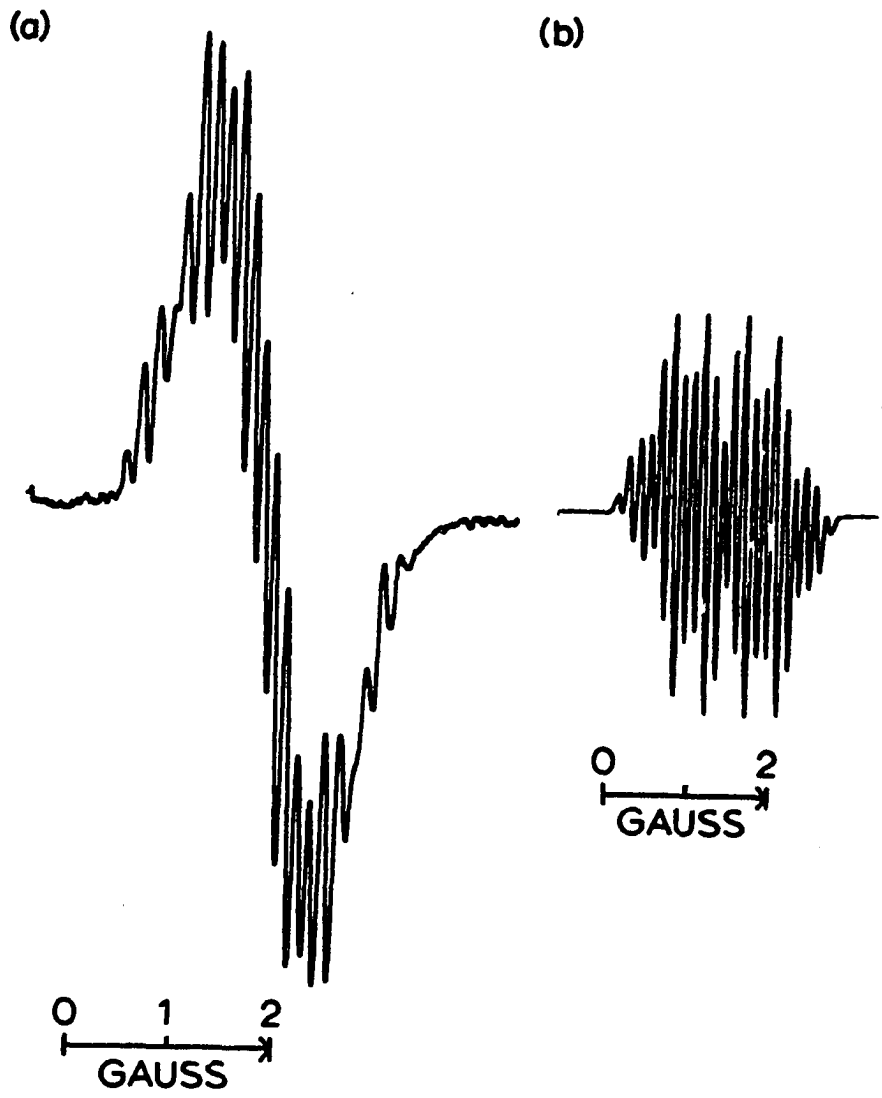


Figure 38. (a) First derivative ESR spectrum of 1,4,4-trimethylbicyclo[3.2.0]hept-6-ene-2,3-semidione (XLII) prepared by the reduction of 1,4,4-trimethylbicyclo[3.2.0]hept-6-en-2,3-dione (0.05 M) in DMSO containing propiophenone (0.02 M) and potassium t-butoxide (0.2 M); (b) simulated spectrum for Lorentzian linewidth of 0.12 gauss and hfsc from text performed by JEOLCO JNM-RA-1 spectrum accumulator.

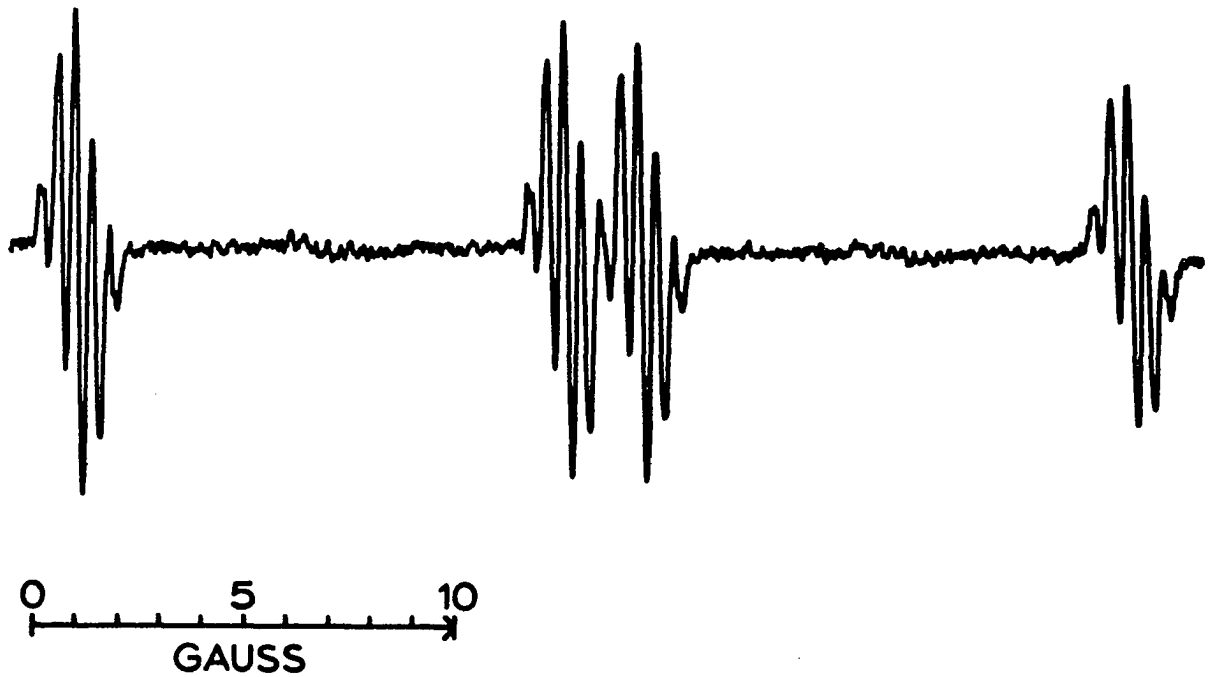


Figure 39. First derivative ESR spectrum of tricyclo[3.3.2.$0^{1,5}$]dec-9-ene-2,3-semidione (XLIII) prepared by the oxidation of tricyclo[3.3.2.$0^{1,5}$]-dec-9-en-2-one (0.1 M) in DMSO containing potassium t-butoxide (0.3 M).

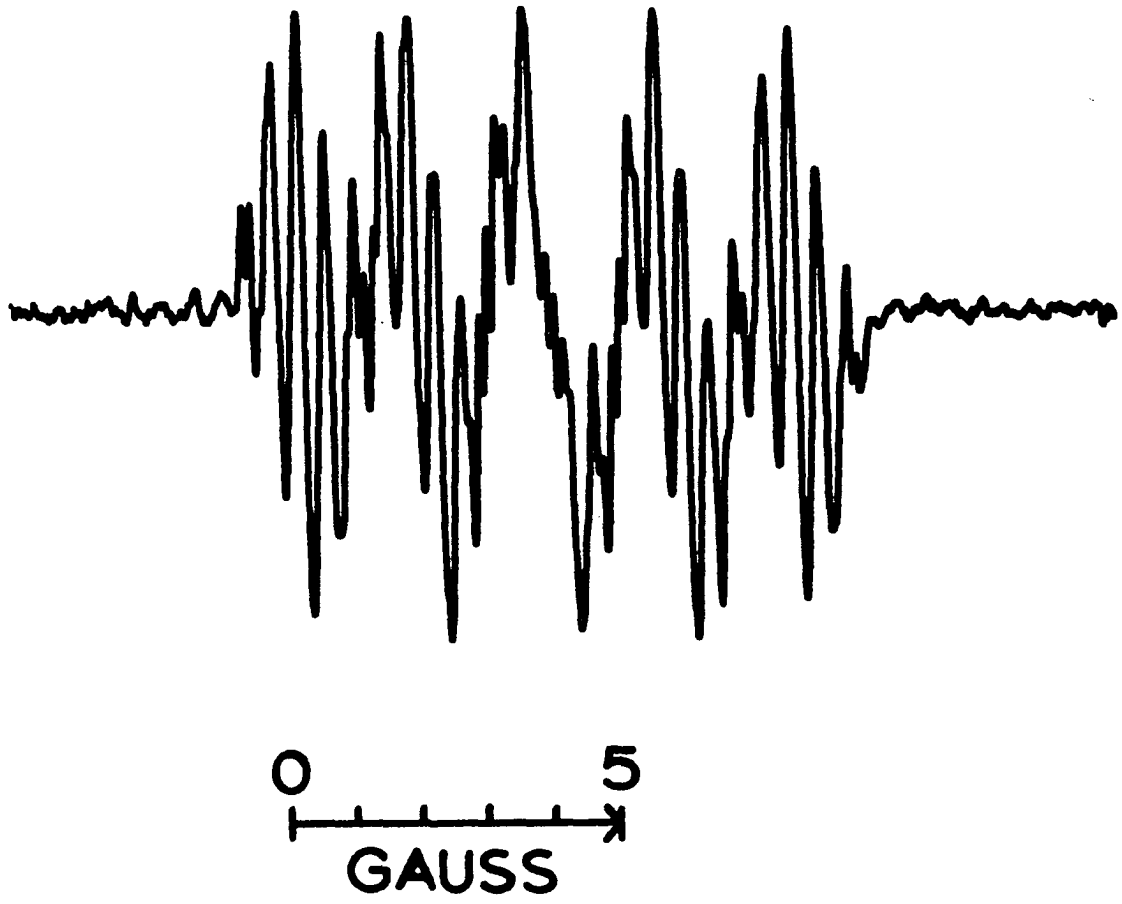


Figure 40. First derivative ESR spectrum of 4,4-dideuteriotricyclo[3.3.2.$0^{1,5}$]dec-9-ene-2,3-semidione prepared by the oxidation of tricyclo[3.3.2.$0^{1,5}$]-dec-9-en-2-one (0.1 M) in d_6-DMSO containing potassium t-butoxide (0.3 M).

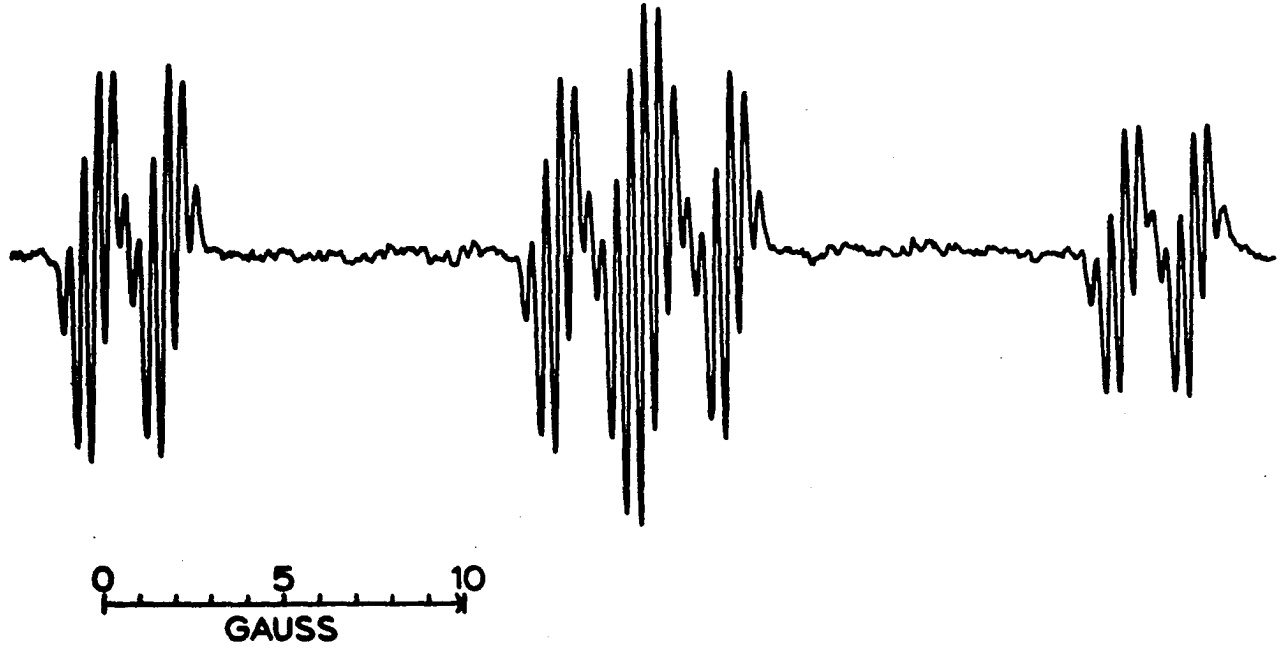


Figure 41. First derivative ESR spectrum of tricyclo[3.3.2.$0^{1,5}$]decane-2,3-semidione (XLIV) prepared by the oxidation of tricyclo[3.3.2.$0^{1,5}$]decan-2-one (0.1 M) in DMSO containing potassium t-butoxide (0.3 M).

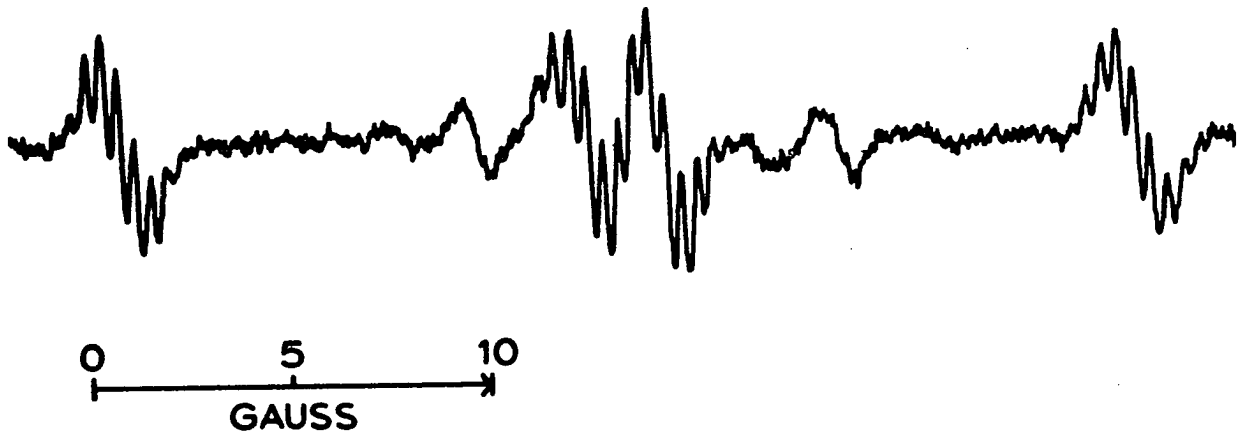


Figure 42. First derivative ESR spectrum of 9,10-dimethyltricyclo[3.3.2.$0^{1,5}$]dec-9-ene-2,3-semidione (XLV) prepared by the oxidation of 9,10-dimethyltricyclo[3.3.2.$0^{1,5}$]dec-9-en-2-one (0.1 M) in DMSO containing potassium t-butoxide (0.3 M).

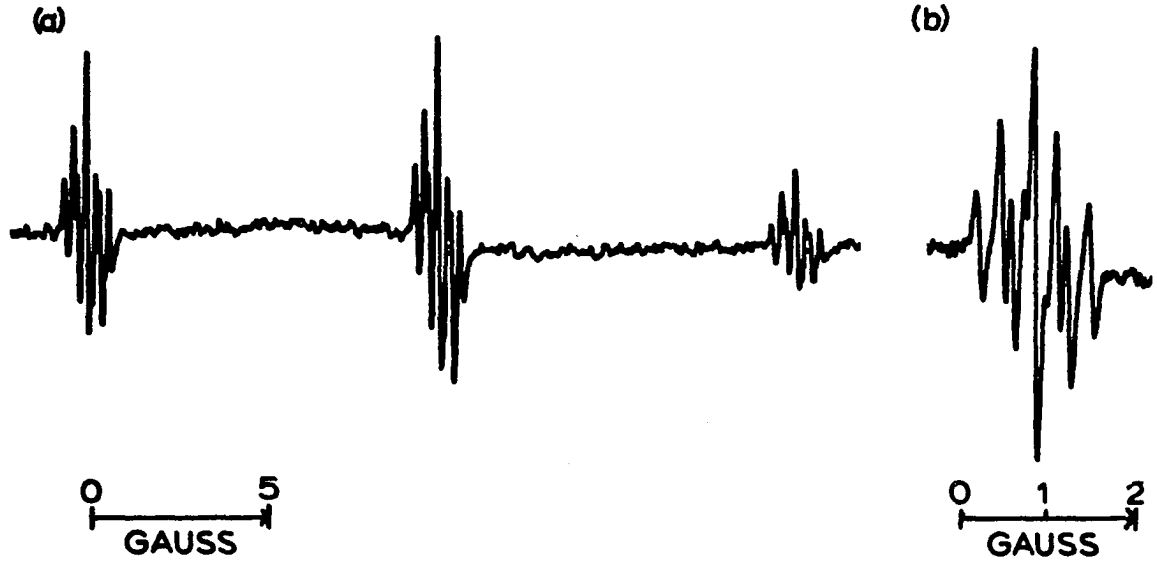


Figure 43. (a) First derivative ESR spectrum of bicyclo[2.1.1]hexane-2,3-semidione (LVI) prepared by the acyloin condensation of 0.2 M dimethyl cis-1,3-cyclobutanedicarboxylate with sodium-potassium alloy in DME, followed by reaction of a filtered aliquot with an equal volume of 0.1 M potassium t-butoxide in DMSO; (b) expansion of the central multiplet of the spectrum shown in (a).

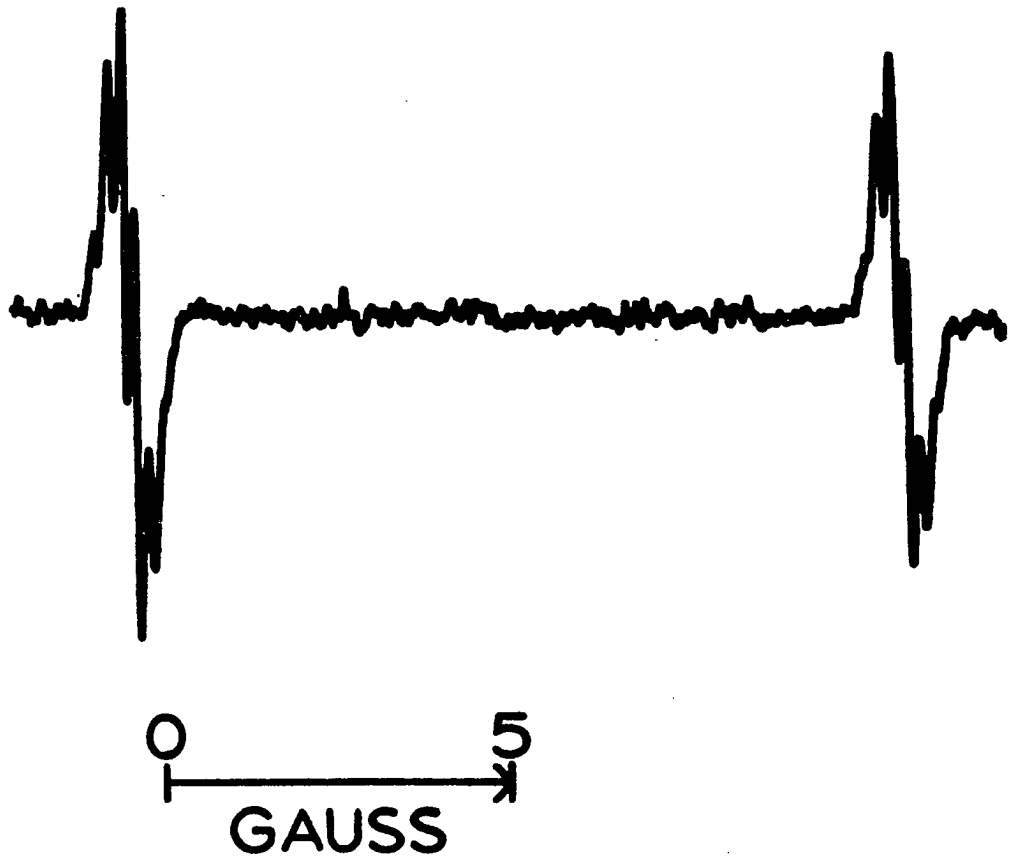


Figure 44. First derivative ESR spectrum of 5,5-dimethylbicyclo[2.1.1]hexane-2,3-semidione (LVIII) prepared by the reaction of the crude 5,5-dimethyl-2,3-bis(trimethylsiloxy)bicyclo[2.1.1]hex-2-ene with potassium t-butoxide in DMSO.

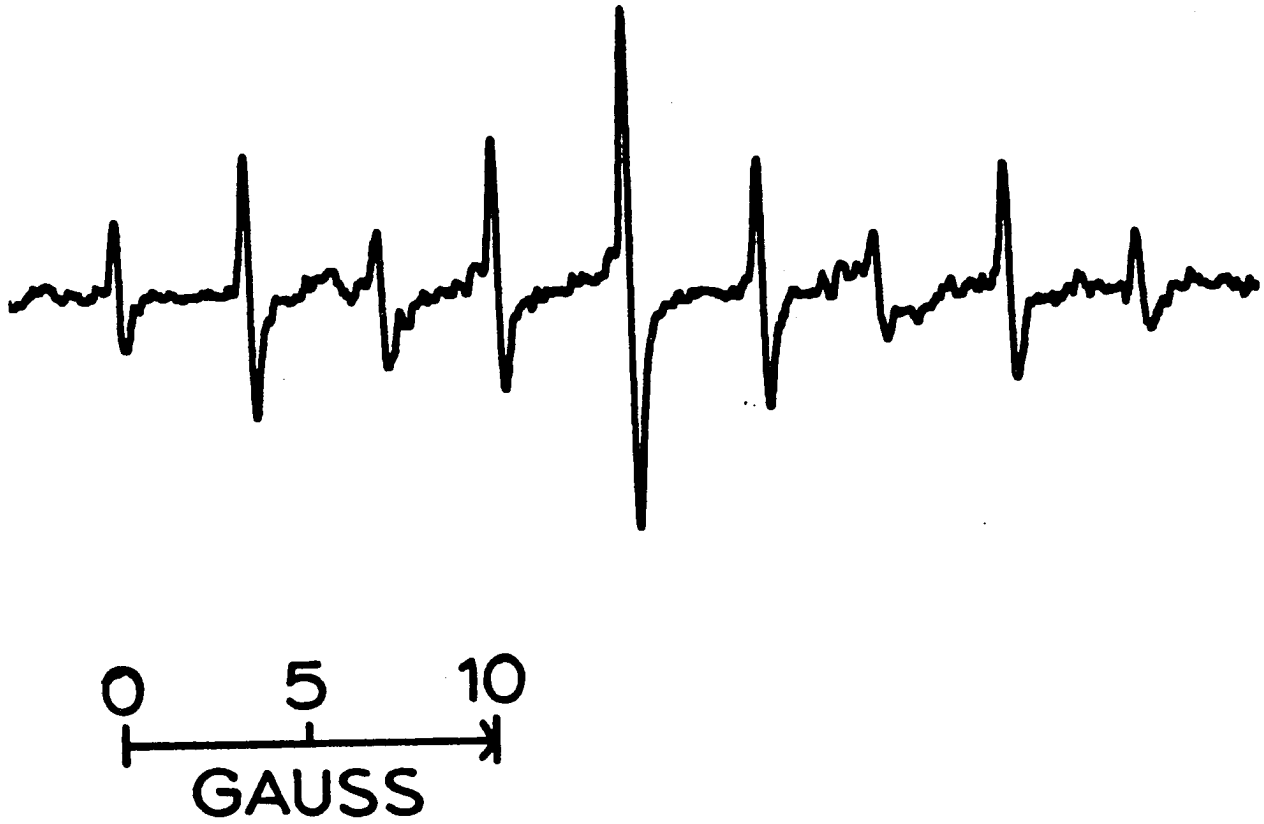


Figure 45. First derivative ESR spectrum of 1,4-dimethylbicyclo[2.1.1]hexane-2,3-semidione (LIX) prepared by the reaction of crude 1,4-dimethyl-2,3-bis(trimethylsiloxy)bicyclo[2.1.1]hex-2-ene with potassium t-butoxide in DMSO.

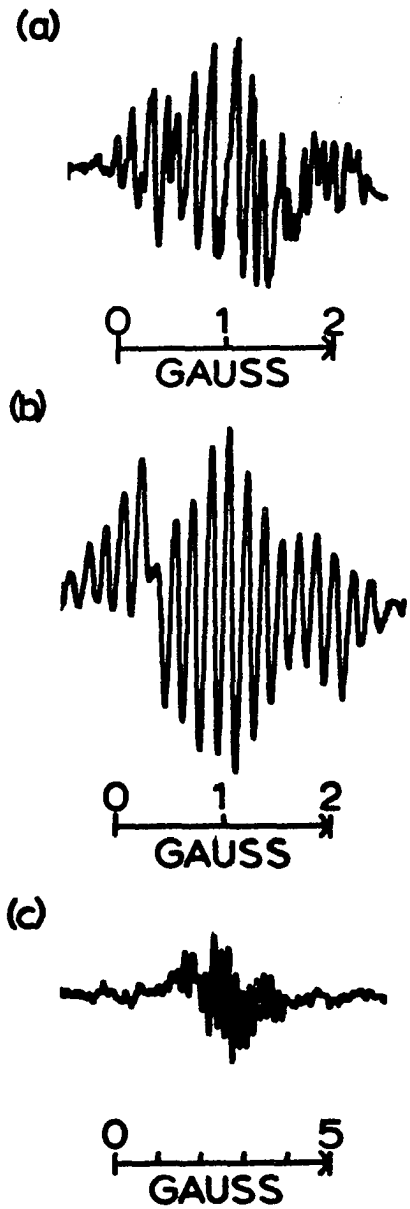


Figure 46. First derivative ESR spectra of tricyclo-[3.3.0.$0^{2,6}$]octane-3,4-semidione (LVII) prepared by the reaction of crude 3,4-bis(trimethylsiloxy) tricyclo[3.3.0.$0^{2,6}$]oct-3-ene with potassium t-butoxide in DMSO [(a), (b) and (c) are the initial spectra from three separate reactions].

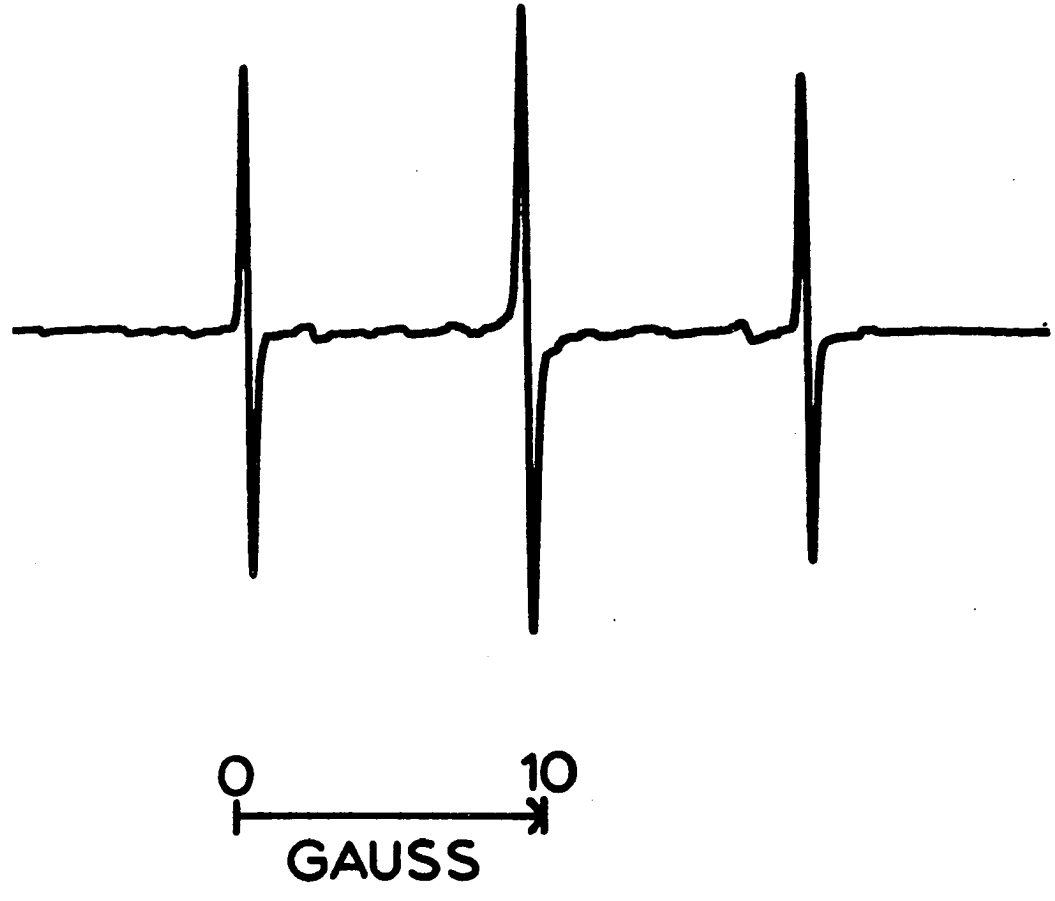


Figure 47. First derivative ESR spectrum of the radical anion produced by the acyloin condensation of dimethyl 2,2,4,4-tetramethyl-cis-1,3-cyclobutanedicarboxylate in ether at 0° in the presence of chlorotrimethylsilane with sodium-potassium alloy, followed by reaction of the crude product with potassium t-butoxide in DMSO.

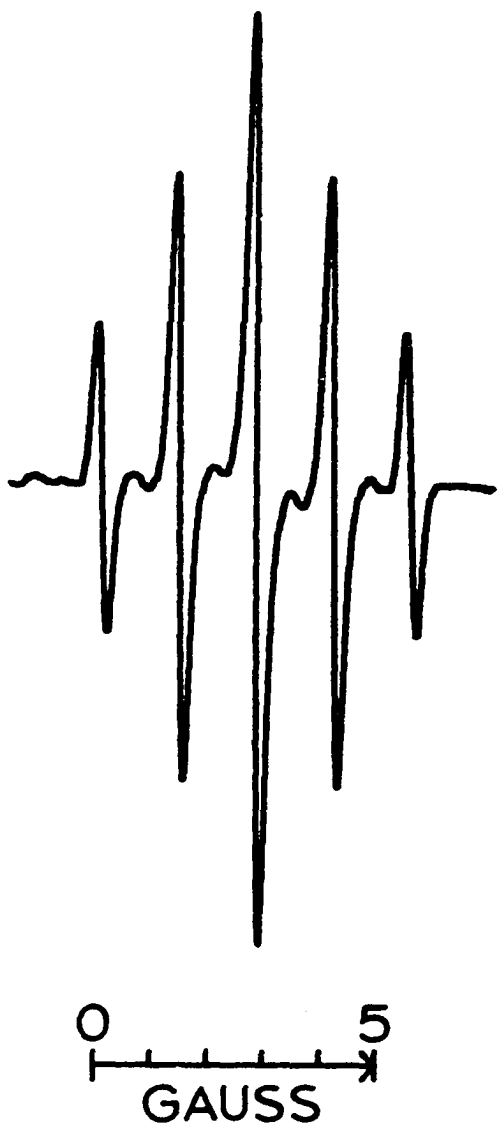


Figure 48. First derivative ESR spectrum of the radical anion produced by the acyloin condensation of dimethyl 2,2,4,4-tetramethyl-cis-1,3-cyclobutanedicarboxylate with sodium-potassium alloy in ether at 0° in the presence of chlorotrimethylsilane, followed by reaction of the crude product with potassium t-butoxide in d_6-DMSO.

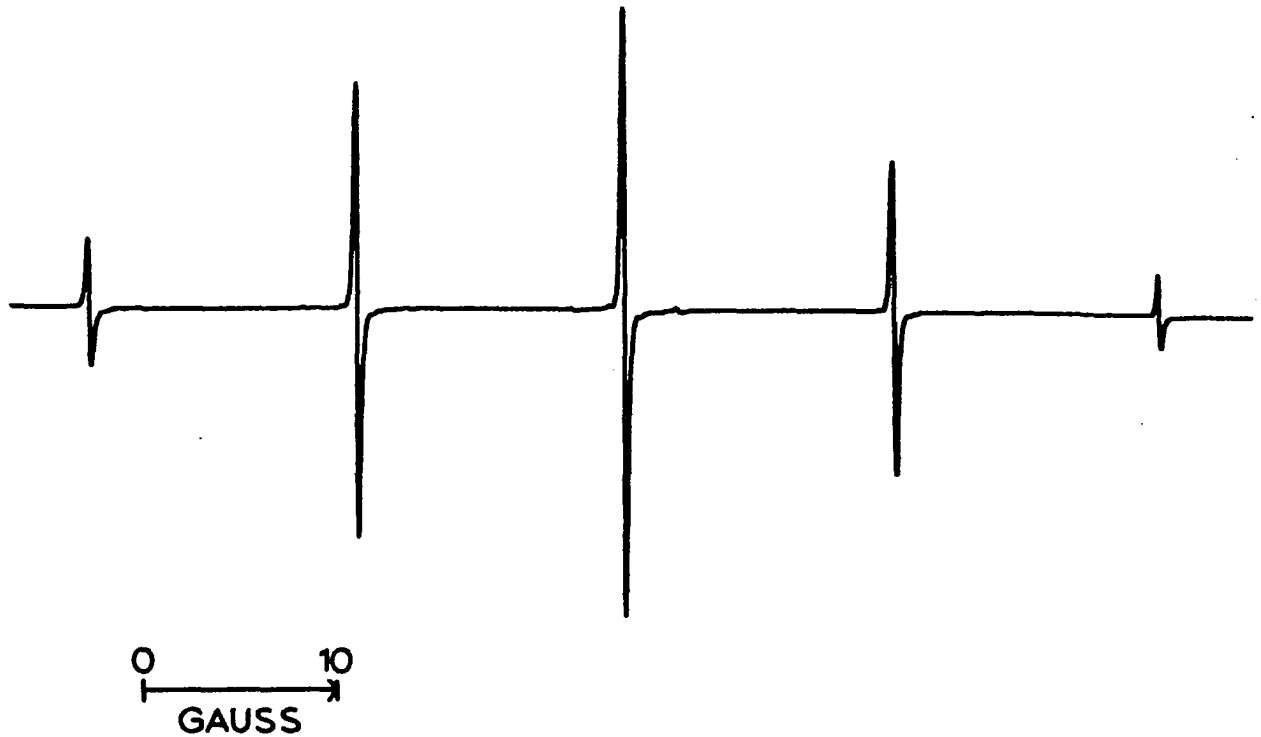


Figure 49. First derivative ESR spectrum of cyclobutanesemidione (LXI) prepared by the reaction of 1,2-bis(trimethylsiloxy)cyclobutene (0.1 M) with potassium t-butoxide (0.2 M) in DMSO.

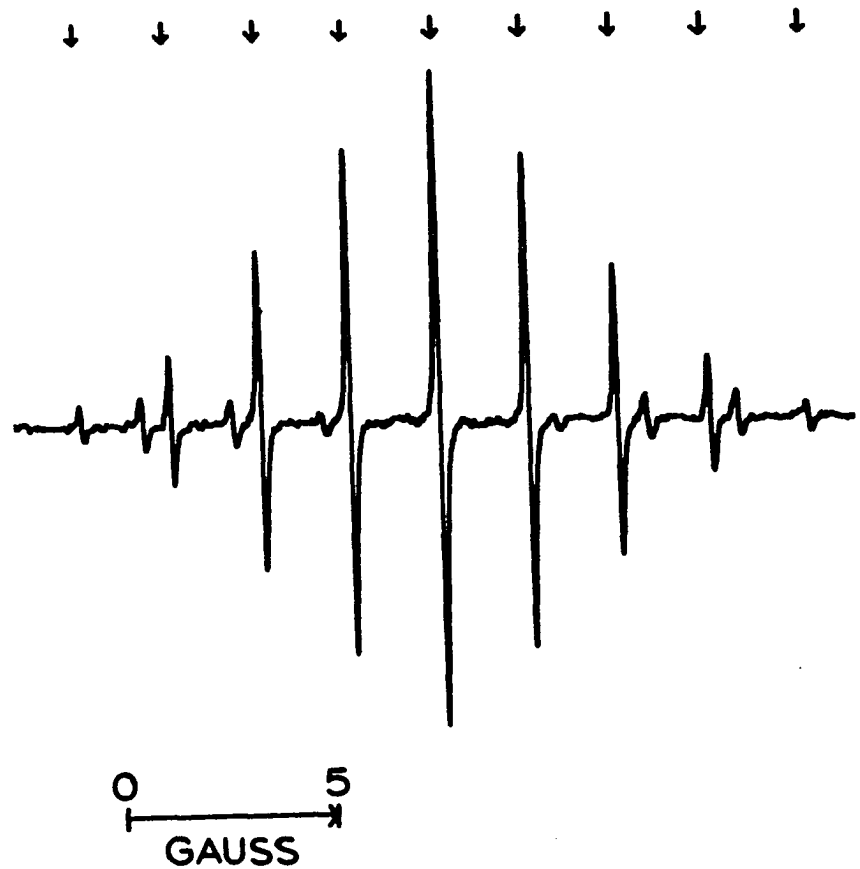


Figure 50. First derivative ESR spectrum of 3,3,4,4-tetradeuteriocyclobutanesemidione prepared by the reaction of 1,2-bis(trimethylsiloxy)cyclobutene (0.2 M) with potassium t-butoxide (0.4 M) in d_6-DMSO (spectrum recorded after 16 hours).

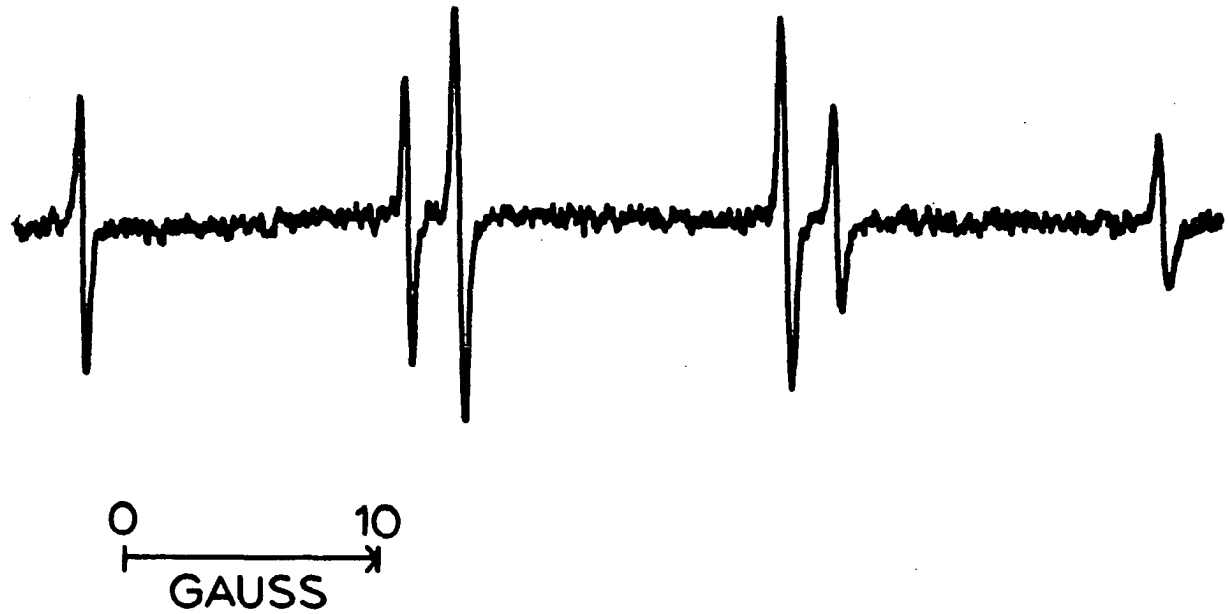


Figure 51. First derivative ESR spectrum of 3-methylcyclobutanesemidione (LXII) prepared by the <u>in situ</u> acyloin condensation of 0.2 M dimethyl α-methylsuccinate with sodium-potassium alloy in DME.

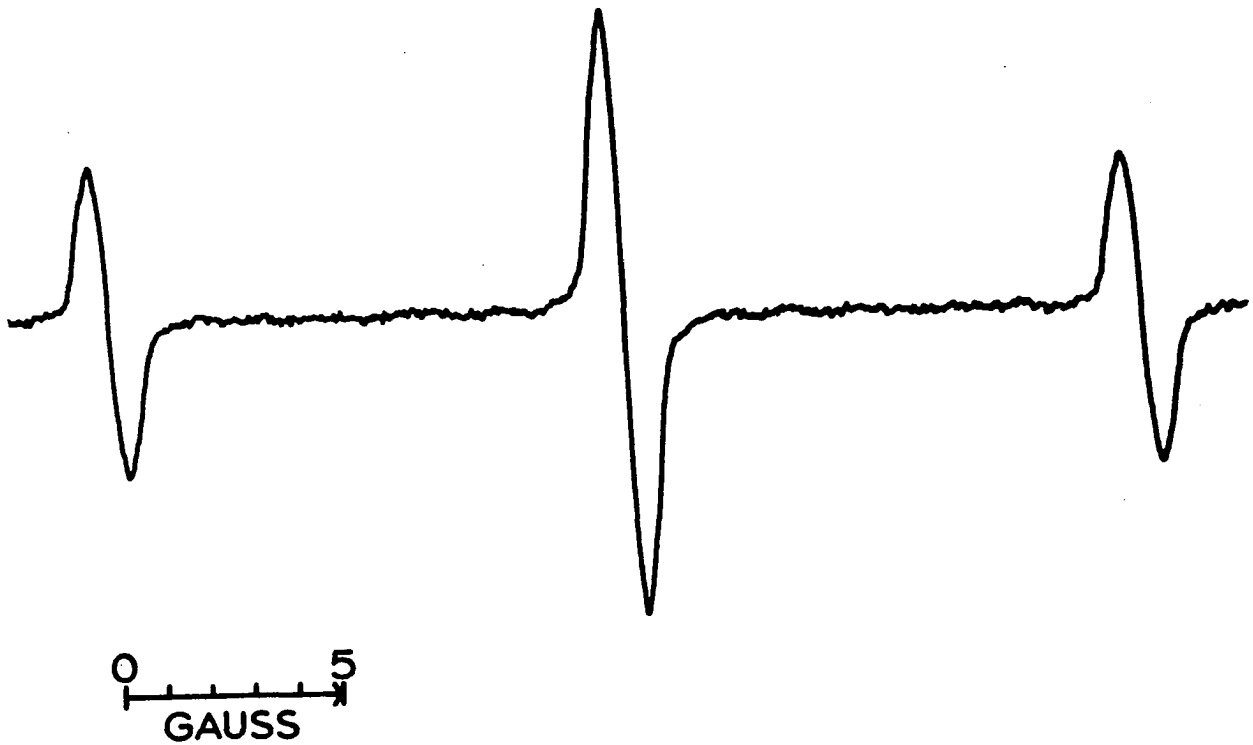


Figure 52. First derivative ESR spectrum of tricyclo[4.2.2.$0^{2,5}$]decane-3,4-semidione (LXIII) prepared by the *in situ* acyloin condensation of 0.2 M dimethyl *cis*-bicyclo[2.2.2]octane-2,3-dicarboxylate with sodium-potassium alloy in DME.

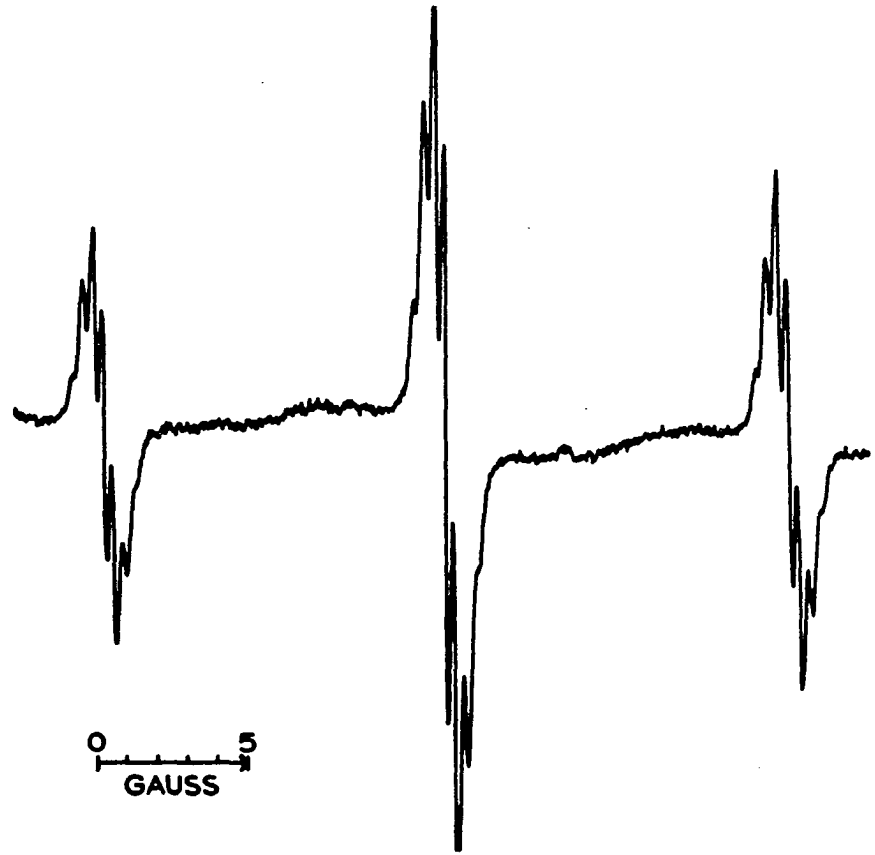


Figure 53. First derivative ESR spectrum of endo-tricyclo[4.2.2.$0^{2,5}$] dec-7-ene-3,4-semidione (LXIV) prepared by the in situ acyloin condensation of 0.2 M dimethyl endo, endo-bicyclo[2.2.2]oct-5-ene-2,3-dicarboxylate with sodium-potassium alloy in DME.

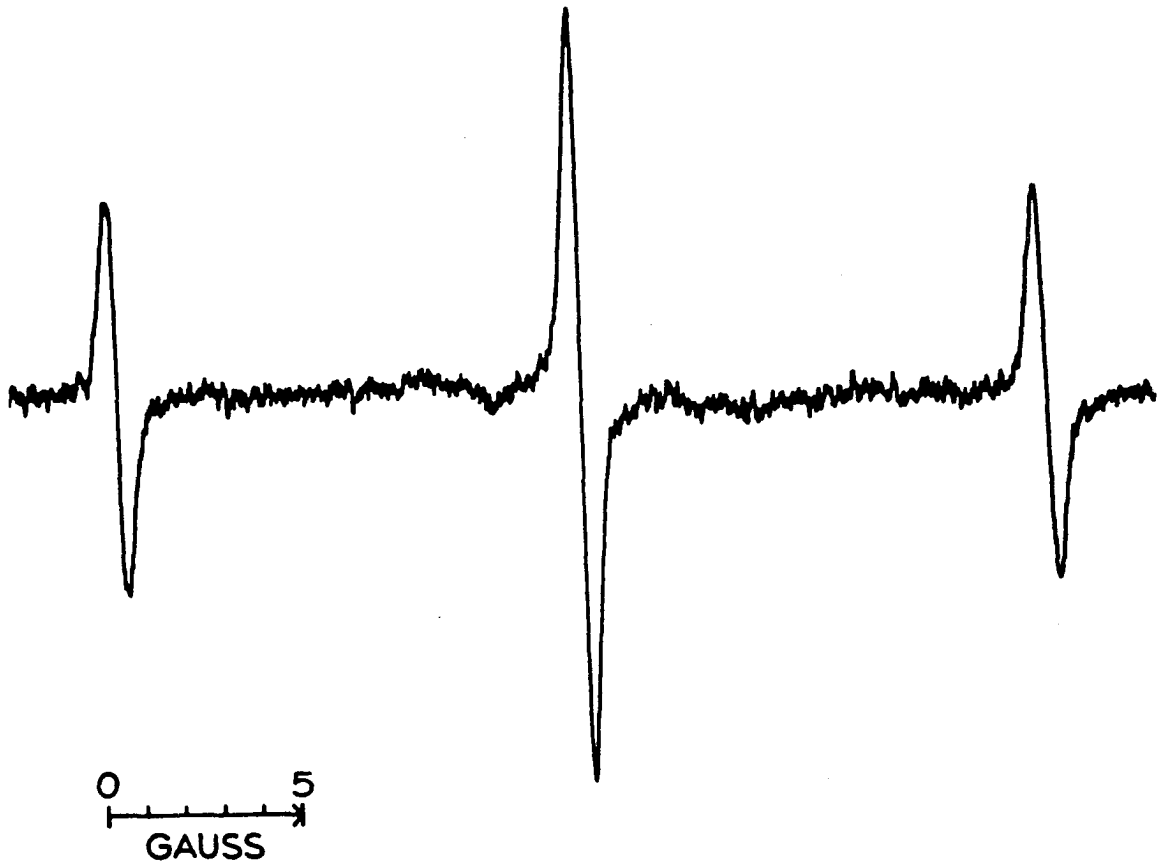


Figure 54. First derivative ESR spectrum of endo, cis, anti-tetracyclo-[4.4.2.$0^{2,5}$.$0.^{7,10}$]dodecane-3,4-semidione (LXV) prepared by the in situ acyloin condensation of 0.2 M dimethyl endo, cis, anti-tricyclo-[4.2.2.$0^{2,5}$]decane-7,8-dicarboxylate with sodium-potassium alloy in DME.

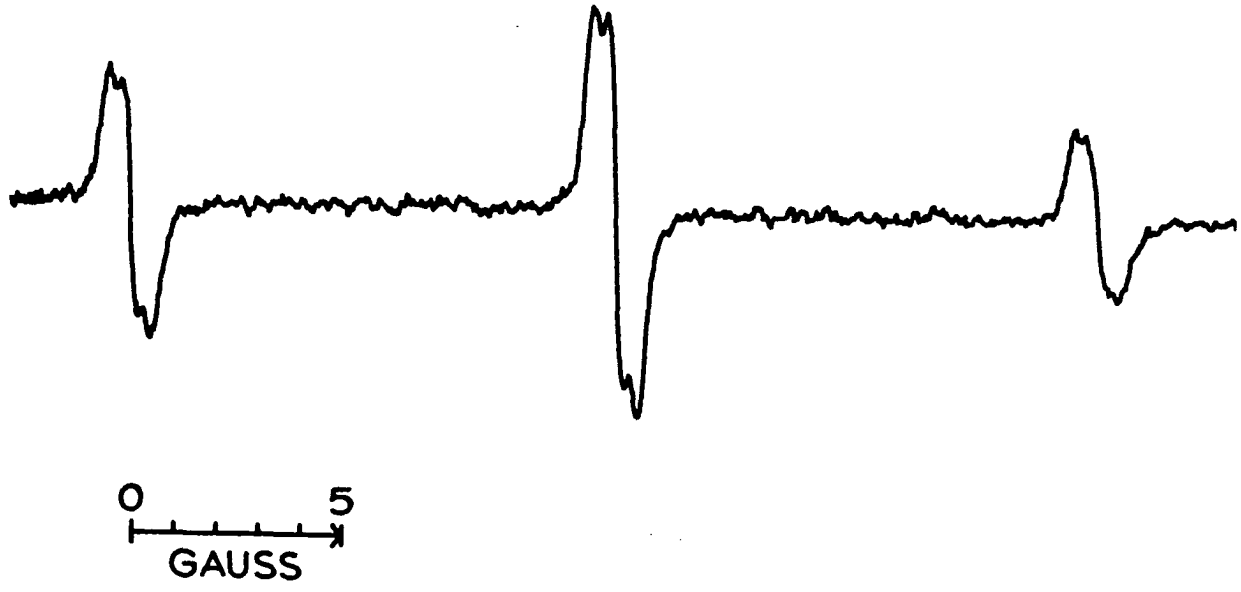


Figure 55. First derivative ESR spectrum of endo, cis, anti-tetracyclo-[4.4.2.$0^{2,5}$.$0^{7,10}$]dodeca-8,11-diene-3,4-semidione (LXVI) prepared by the in situ acyloin condensation of 0.2 M dimethyl endo, cis, anti-tricyclo[4.2.2.$0^{2,5}$]deca-3,9-diene-7,8-dicarboxylate with sodium-potassium alloy in DME.

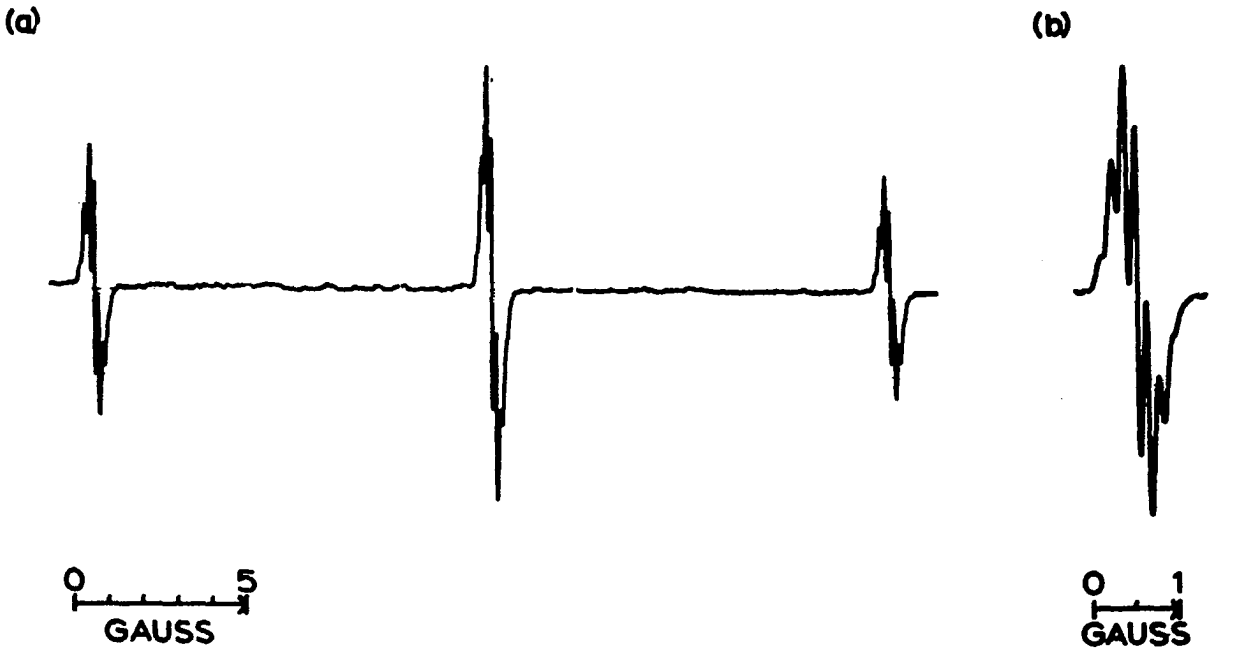


Figure 56. (a) First derivative ESR spectrum of endo-hexacyclo[4.4.2.$0^{2,5}$.$0^{7,10}$.-$0^{9,11}$.$0^{8,12}$]dodecane-3,4-semidione (LXVII) prepared by the reaction of the corresponding crude bis(trimethylsiloxy)alkene with potassium t-butoxide in DMSO; (b) expansion of central multiplet of spectrum in (a).

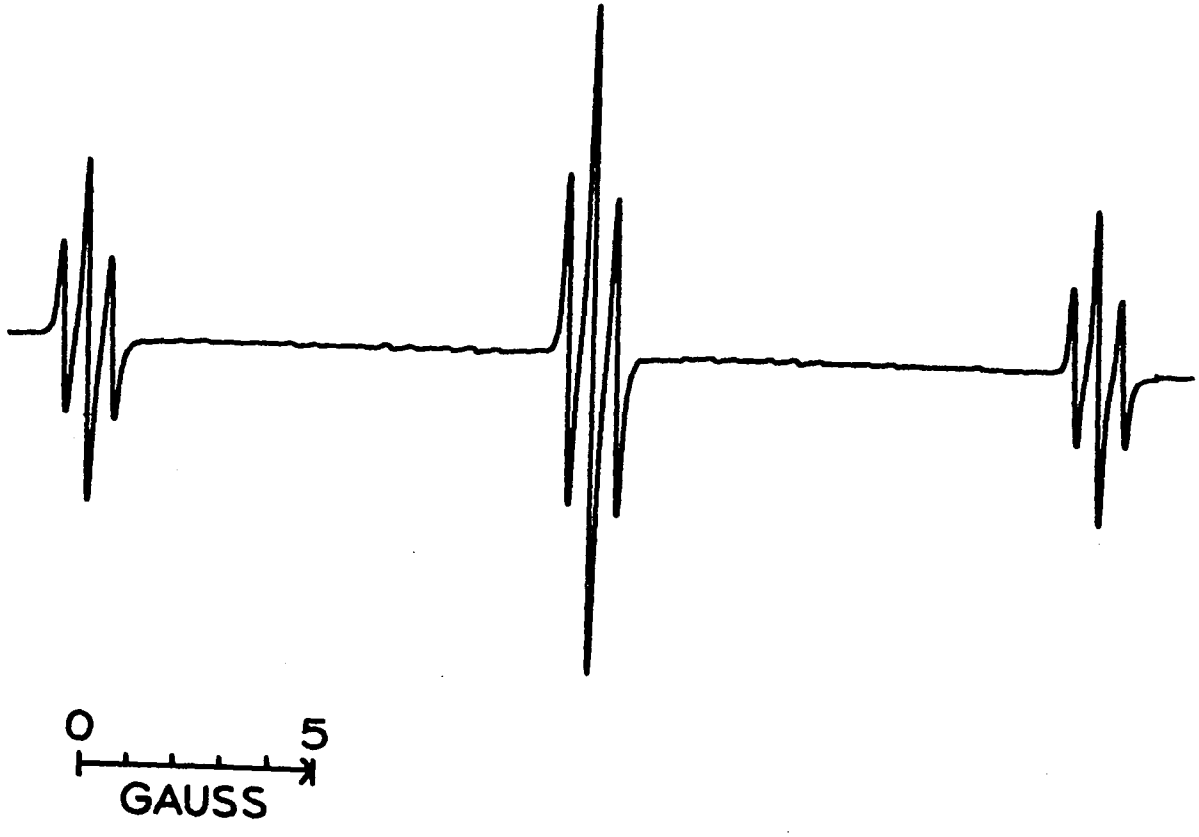


Figure 57. First derivative ESR spectrum of 7,8; 9,10-dibenzotricyclo-[4.2.2.$0^{2,5}$]deca-7,9-diene-3,4-semidione (LXVIII) prepared by the reaction of crude 3,4-bis(trimethylsiloxy)-7,8;9,10-dibenzotricyclo-[4.2.2.$0^{2,5}$]deca-3,7,9-triene with potassium t-butoxide in DMSO.

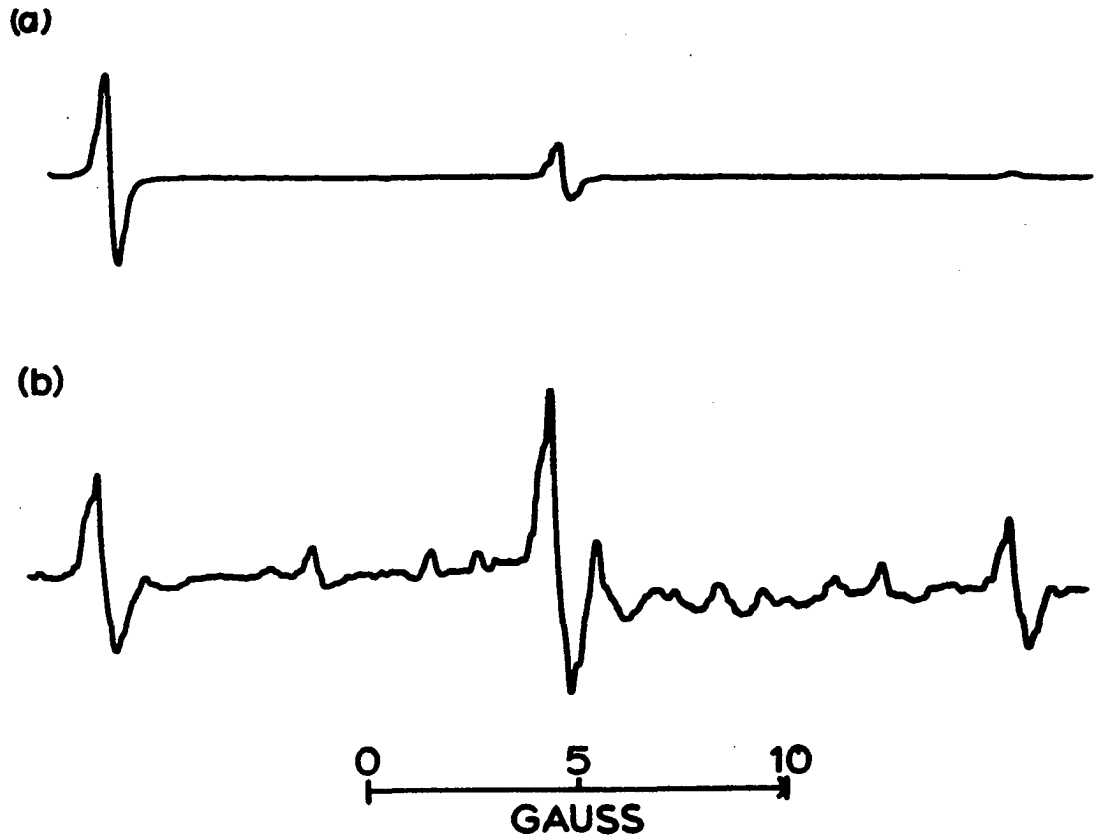


Figure 58. First derivative ESR spectra of 1,6-dideuterio-7,8;9,10-dibenzotricyclo-[4.2.2.$0^{2,5}$]deca-7,9-diene-3,4-semidione (LXIX) prepared by reacting the corresponding crude bis(trimethylsiloxy)alkene with potassium t-butoxide in DMSO [(a) and (b) are the initially recorded spectra from two separate reactions].

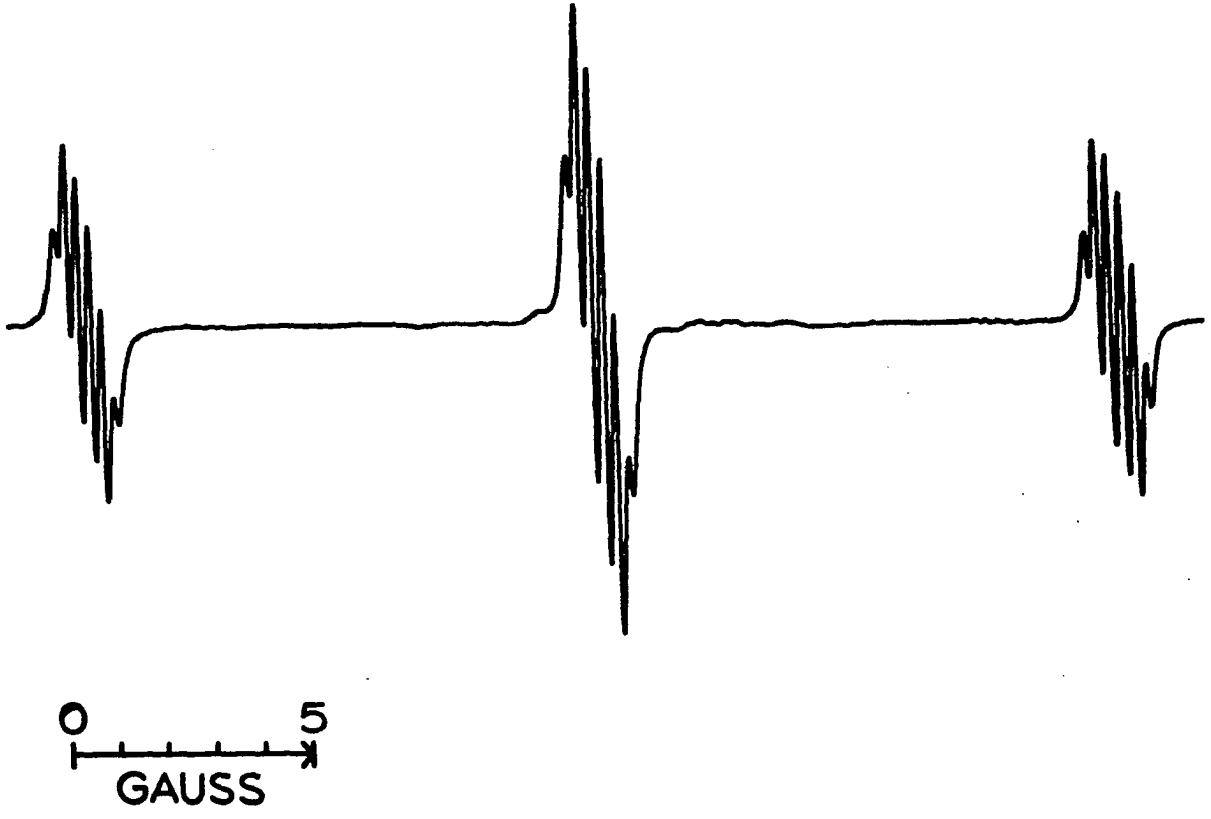


Figure 59. First derivative ESR spectrum of 1-methyl-7,8; 9,10-dibenzotricyclo-[4.2.2.$0^{2,5}$]deca-7,9-diene-3,4-semidione (LXX) prepared by the reaction of the corresponding crude bis(trimethylsiloxy)alkene with potassium t-butoxide in DMSO.

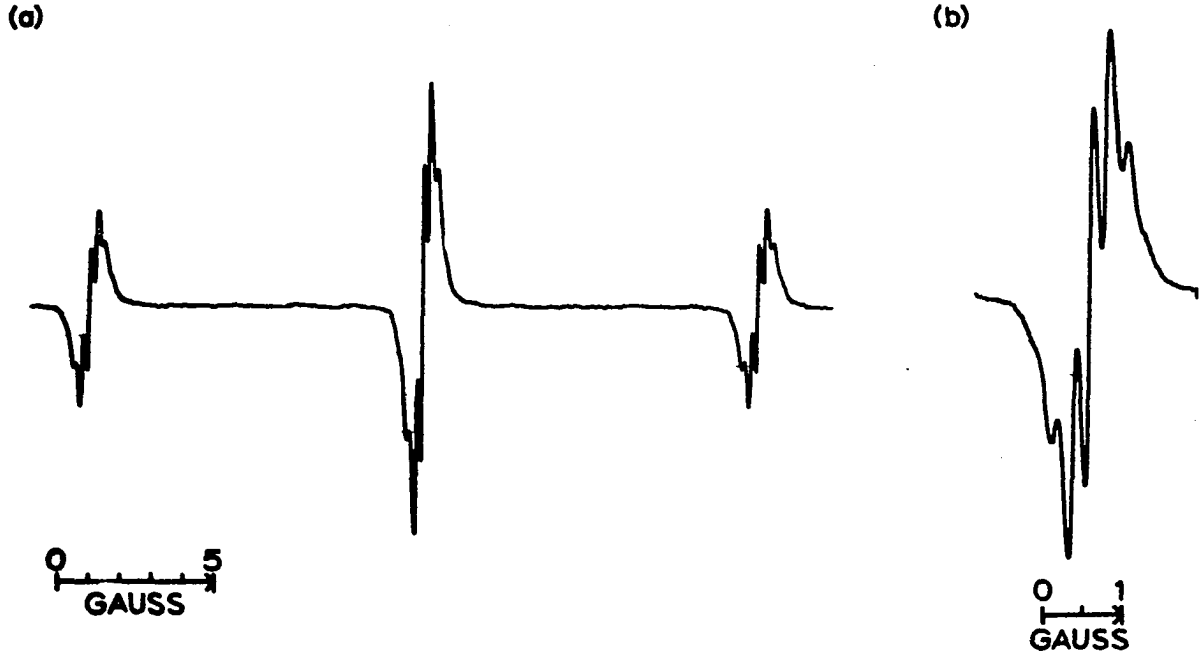


Figure 60. (a) First derivative ESR spectrum of 1,6-dimethyl-7,8; 9,10-dibenzo-tricyclo[4.2.2.$0^{2,5}$]deca-7,9-diene-3,4-semidione (LXXI) prepared by the reaction of the corresponding crude bis(trimethylsiloxy)alkene with potassium t-butoxide in DMSO; (b) expansion of central multiplet of spectrum in (a).

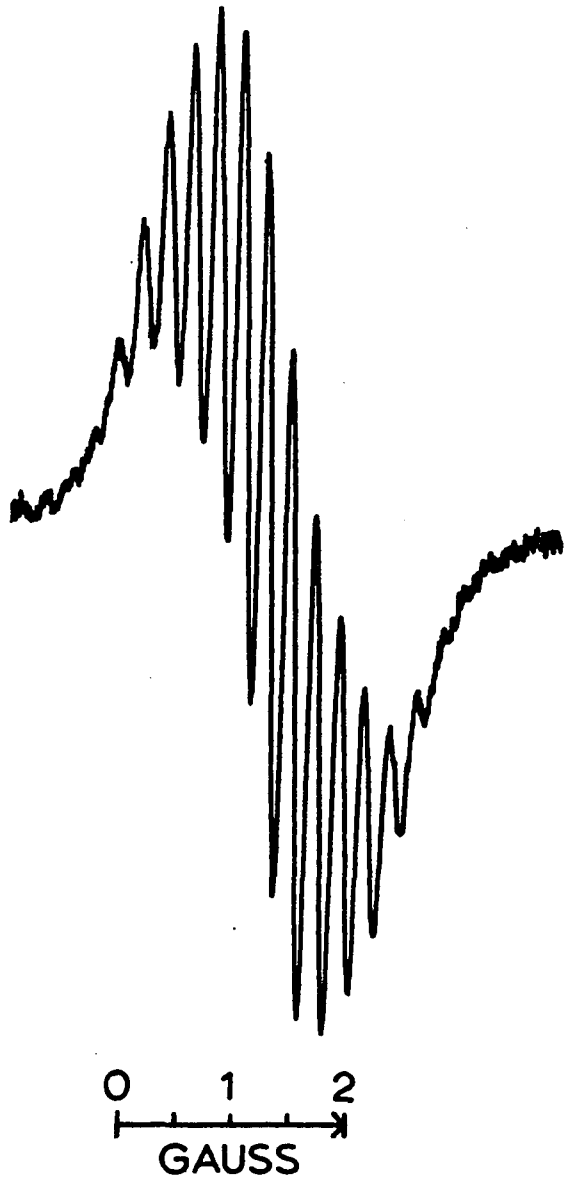


Figure 61. First derivative ESR spectrum of exo, exo-2,5-dimethyltricyclo[4.2.2.$0^{2,5}$]dec-7-ene-3,4-semidione (LXXII) prepared by the in situ acyloin condensation of dimethyl exo, exo-2,3-dimethylbicyclo-[2.2.2]oct-5-ene-endo, endo-2,3-dicarboxylate with sodium-potassium alloy in DME.

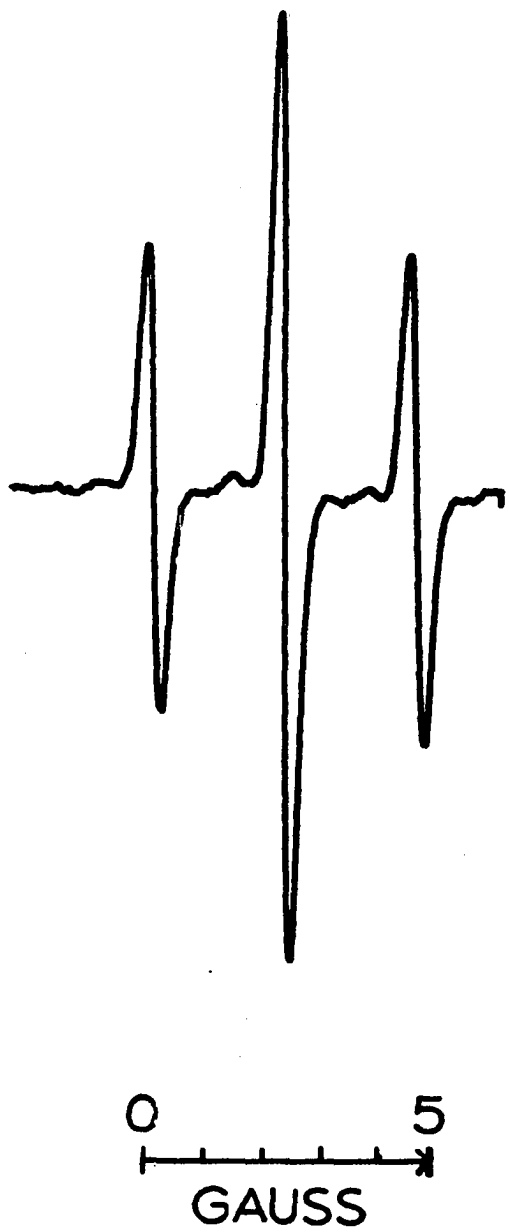


Figure 62. First derivative ESR spectrum of anti-tricyclo-[4.2.2.$0^{2,5}$]decane-7,8-semidione (LXXIII) prepared by the reaction of the corresponding crude bis(trimethylsiloxy)alkene with potassium t-butoxide in DMSO.

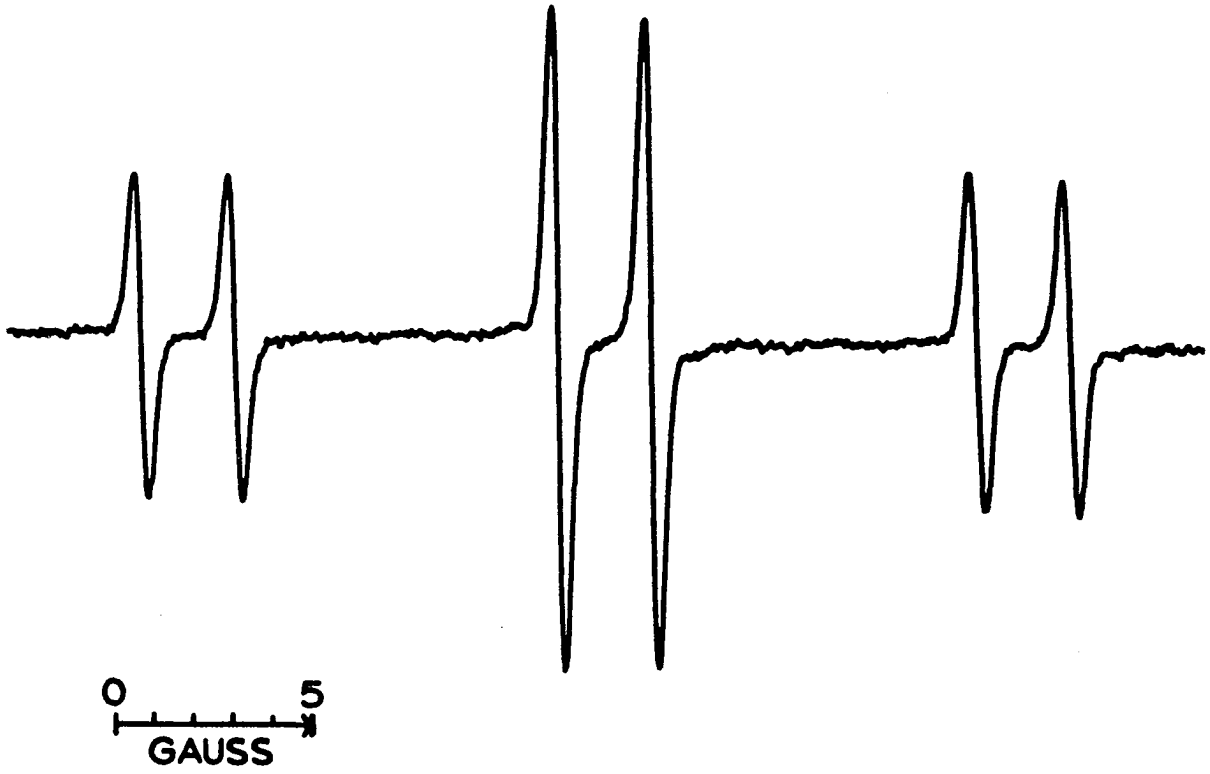


Figure 63. First derivative ESR spectrum of endo-tricyclo[4.2.1.$0^{2,5}$]nonane-3,4-semidione (LXXX) prepared by the in situ acyloin condensation of 0.2 M dimethyl endo, endo-2,3-norbornanedicarboxylate with sodium-potassium alloy in DME.

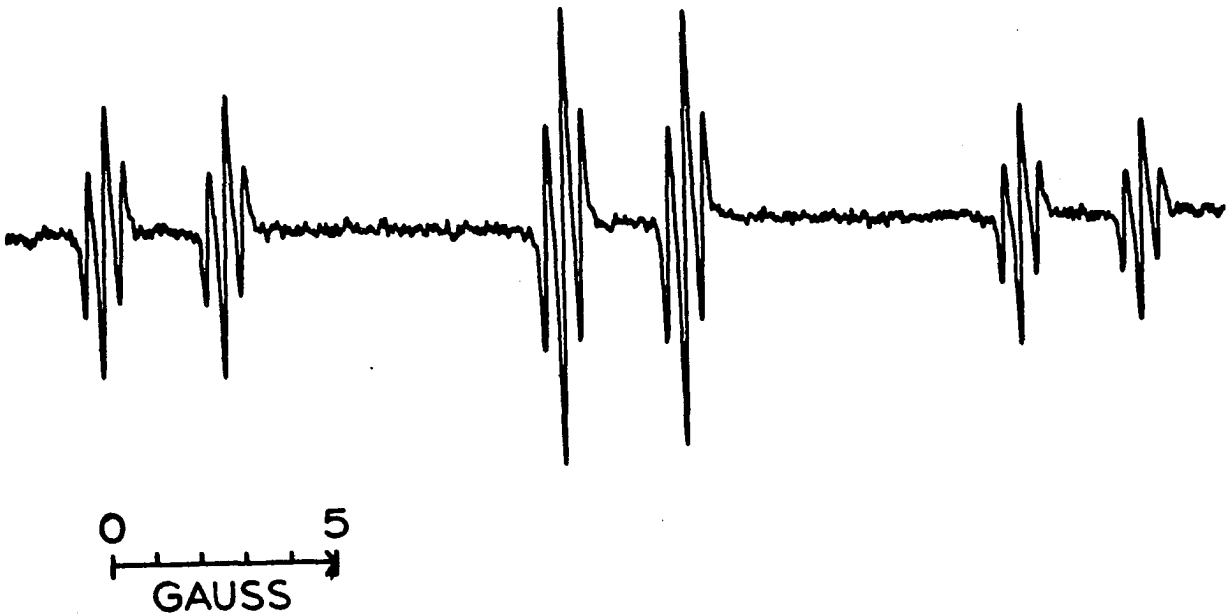


Figure 64. First derivative ESR spectrum of endo-tricyclo[4.2.1.$0^{2,5}$]non-7-ene-3,4-semidione (LXXXI) prepared by the in situ acyloin condensation of 0.2 M dimethyl 5-norbornene-endo, endo-2,3-dicarboxylate with sodium-potassium alloy in DME.

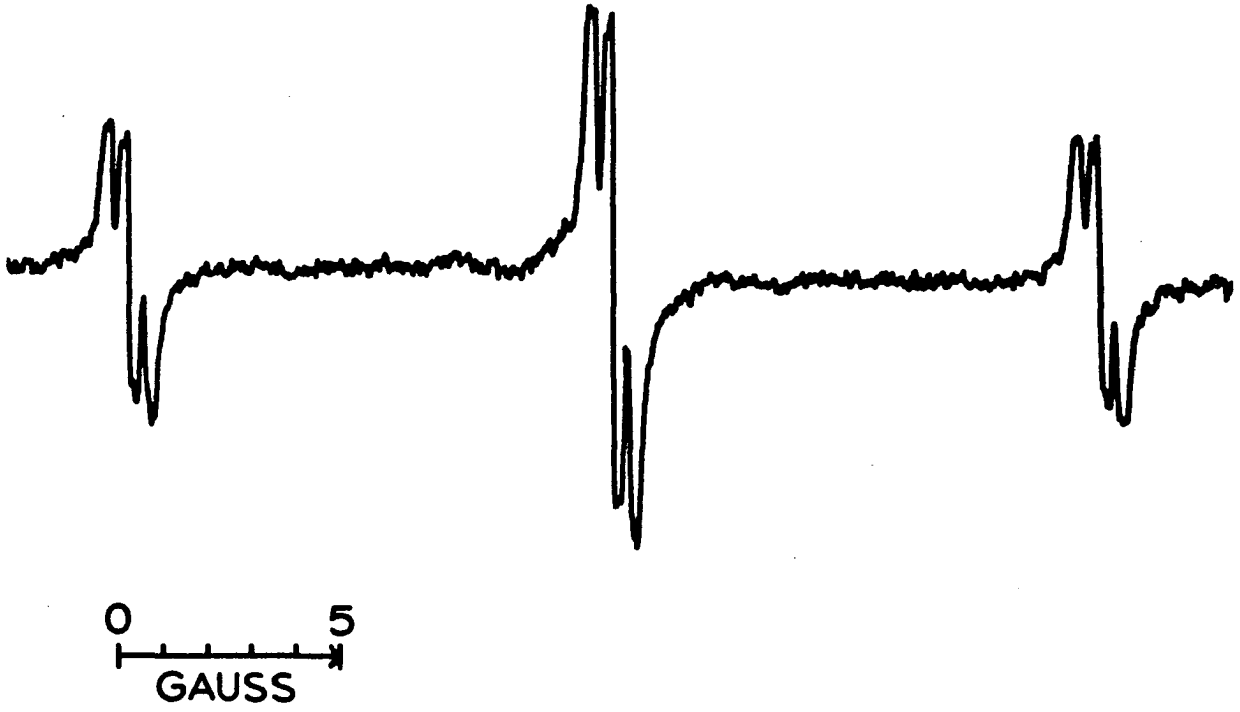


Figure 65. First derivative ESR spectrum of endo-pentacyclo[4.3.1.1^{8,10} 0^{2,5}.-0^{7,9}]undecane-3,4-semidione (LXXXII) prepared by the in situ acyloin condensation of 0.2 M dimethyl tetracyclo[3.2.1.1^{3,8}.0^{2,4}]nonane-endo, endo-6,7-dicarboxylate with sodium-potassium alloy in DME.

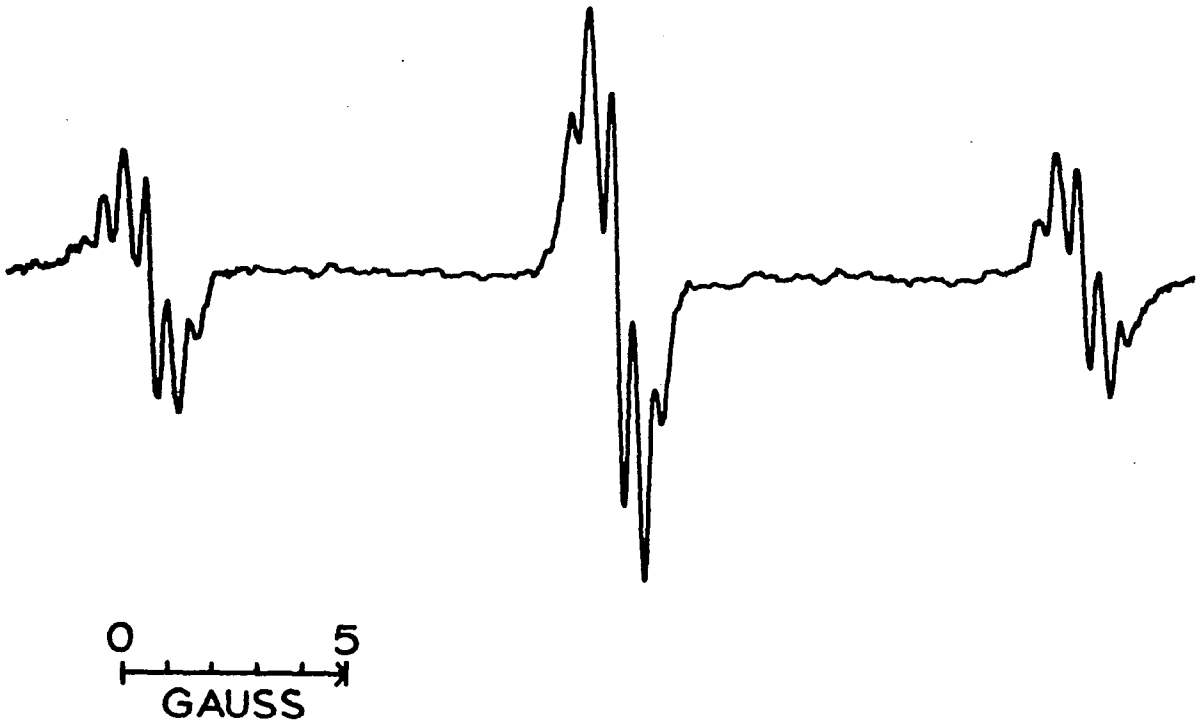


Figure 66. First derivative ESR spectrum of exo-tricyclo[4.2.1.$0^{2,5}$]non-7-ene-3,4-semidione (LXXXIII) prepared by the in situ acyloin condensation of 0.2 M dimethyl 5-norbornene-exo, exo-2,3-dicarboxylate with sodium-potassium alloy in DME.

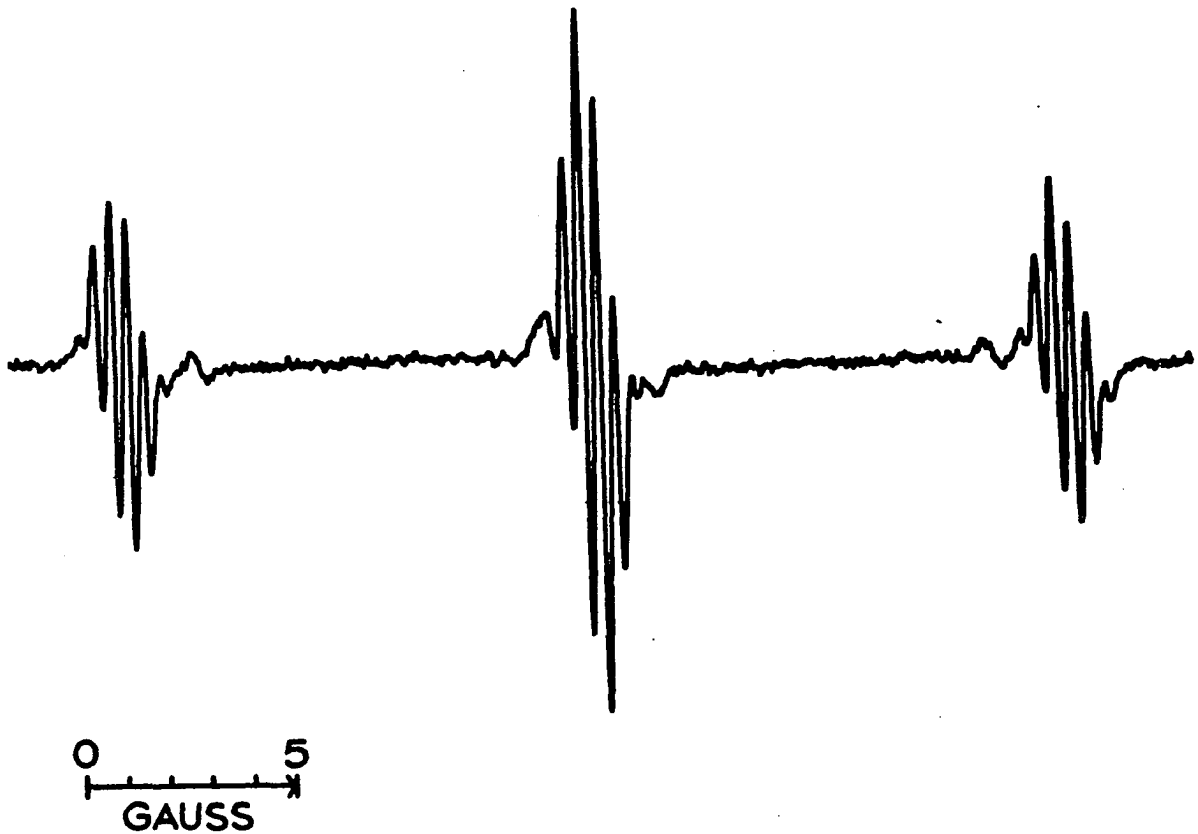


Figure 67. First derivative ESR spectrum of exo-tricyclo[4.2.1.$0^{2,5}$]nonane-3,4-semidione (LXXXIV) prepared by the in situ acyloin condensation of 0.2 M dimethyl exo, exo-2,3-norbornanedicarboxylate with sodium-potassium alloy in DME.

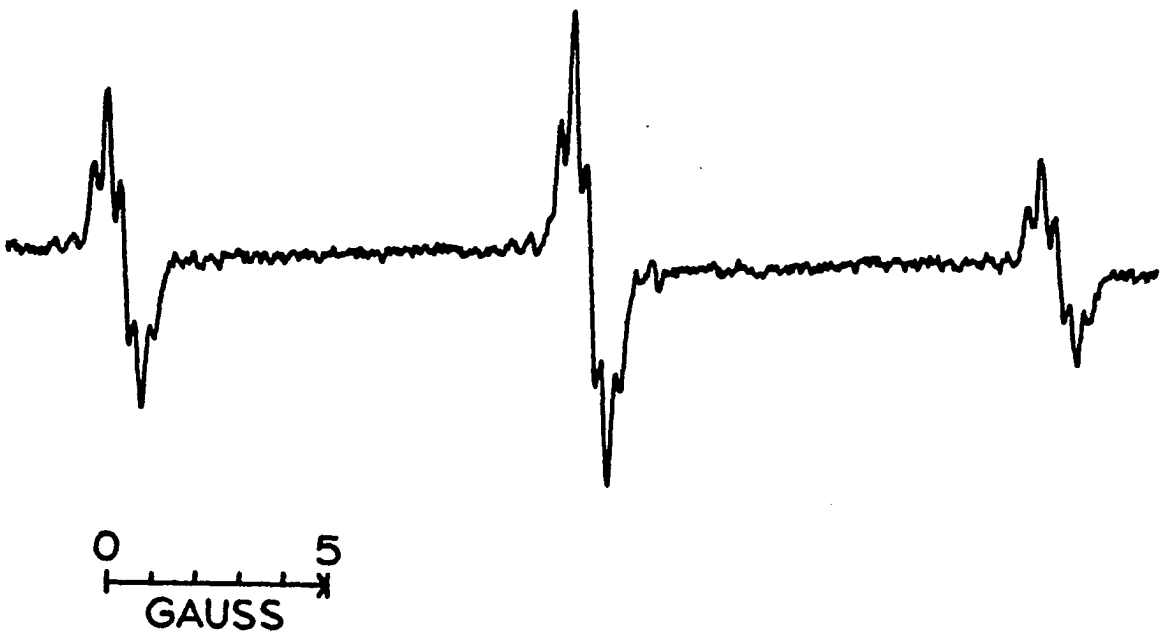


Figure 68. First derivative ESR spectrum of exo, exo-7,8-dideuterio-exo-tricyclo-[4.2.1.$0^{2,5}$]nonane-3,4-semidione (LXXXV) prepared by the in situ acyloin condensation of 0.2 M dimethyl exo, exo-5,6-dideuterionorbornane-exo, exo-2,3-dicarboxylate with sodium-potassium alloy in DME.

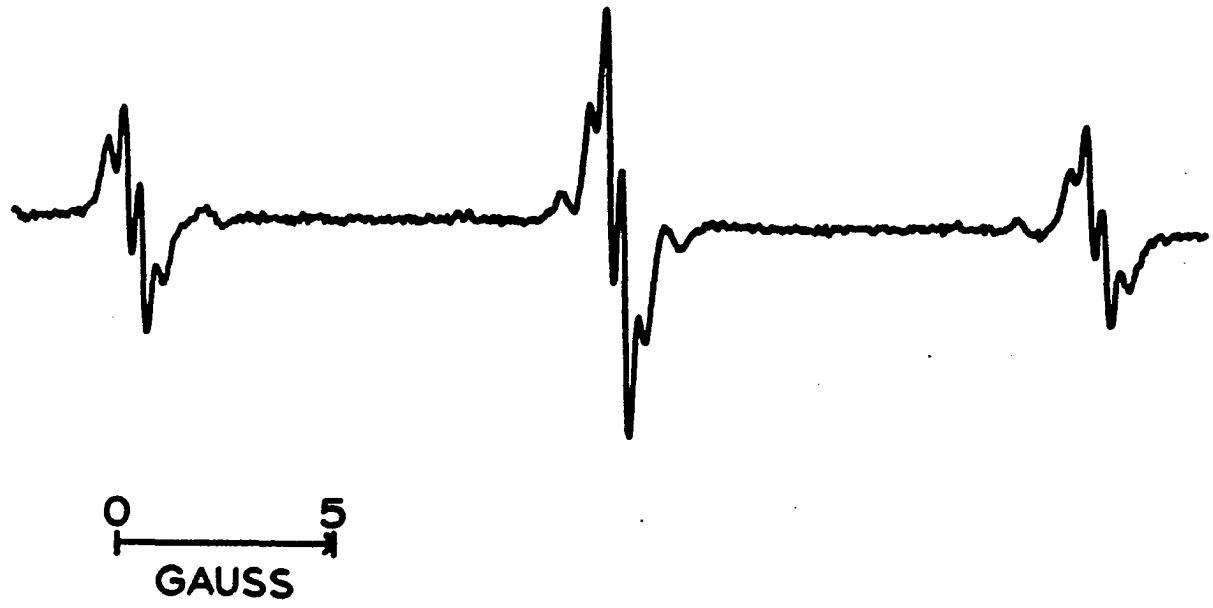


Figure 69. First derivative ESR spectrum of 7-isopropylidine-exo-tricyclo[4.2.1.$0^{2,5}$]-nonane-3,4-semidione (LXXXVI) prepared by the in situ acyloin condensation of 0.2 M dimethyl 7-isopropylidine-exo, exo-2,3-norbornanedicarboxylate with sodium-potassium alloy in DME.

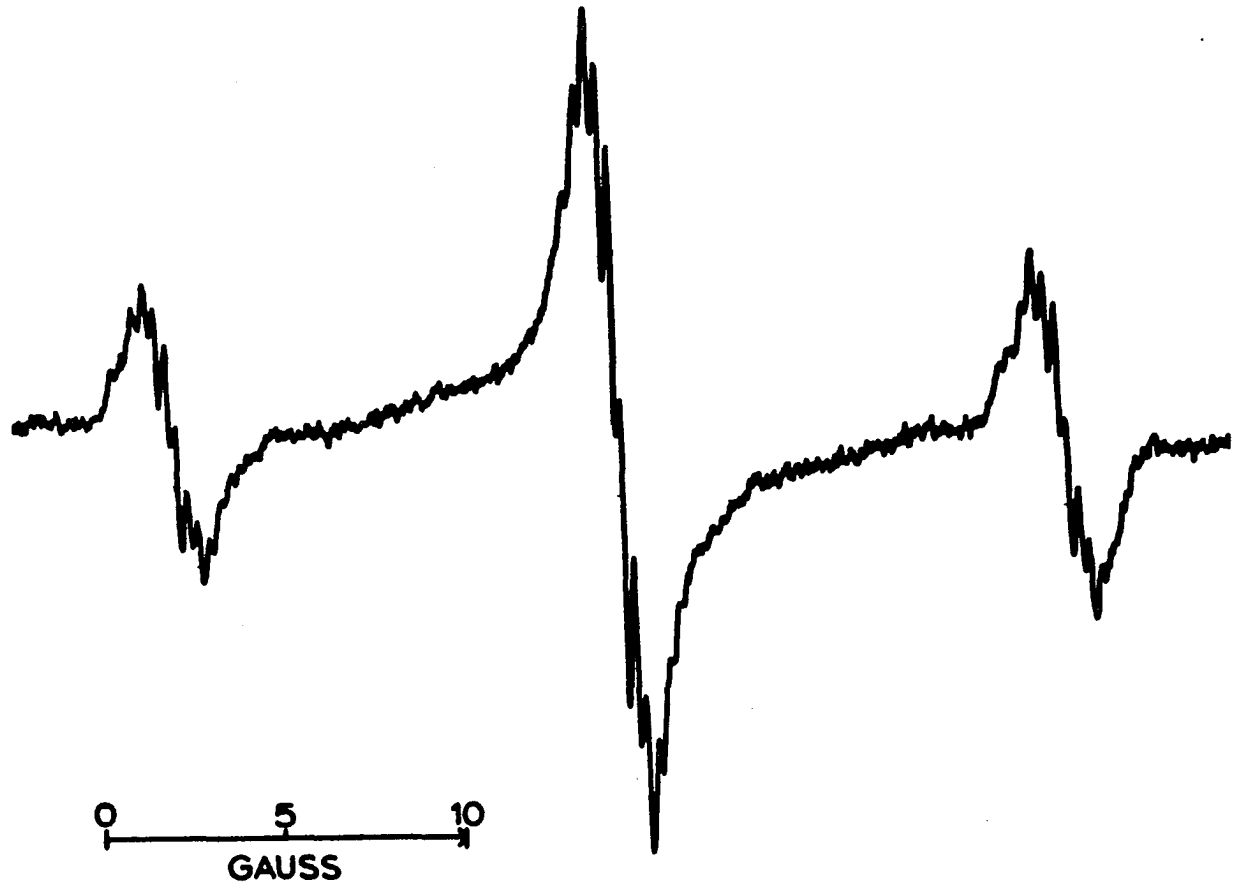


Figure 70. First derivative ESR spectrum of endo-tricyclo[4.3.2.$0^{2,5}$]undec-10-ene-3,4-semidione (LXXXVII) prepared by the in situ acyloin condensation of dimethyl bicyclo[3.2.2]non-8-ene-endo, endo-6,7-dicarboxylate with sodium-potassium alloy in DME.

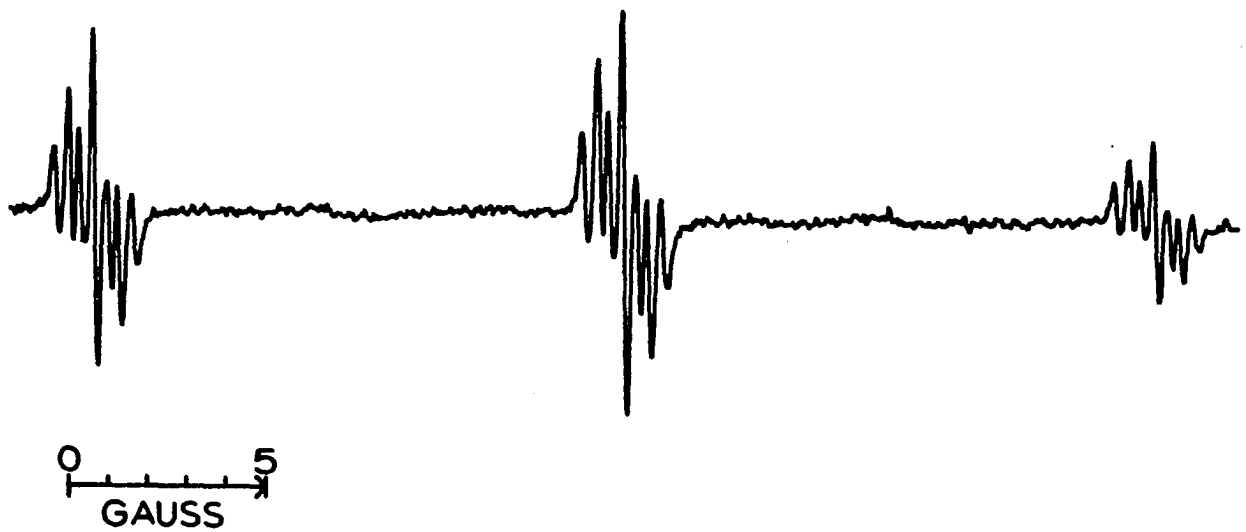


Figure 71. First derivative ESR spectrum of cis-bicyclo[4.2.0]oct-3-ene-7,8-semidione (XCII) prepared by the in situ acyloin condensation of dimethyl cis-cyclohex-4-ene-1,2-dicarboxylate with sodium-potassium alloy in DME.

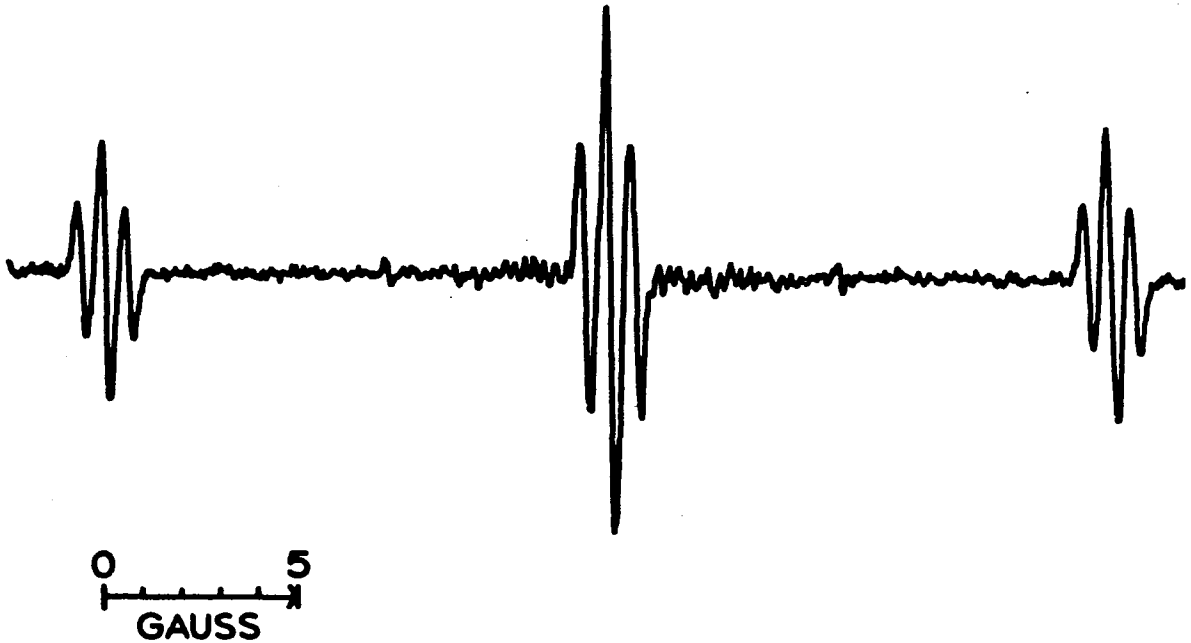


Figure 72. First derivative ESR spectrum of cis-3,4-dimethylbicyclo[4.2.0]oct-3-ene-7,8-semidione (XCIII) prepared by the reaction of cis-3,4-dimethyl-7,8-bis(trimethylsiloxy)bicyclo[4.2.0]octa-3,7-diene (0.1 M) with potassium t-butoxide (0.2 M) in DMSO.

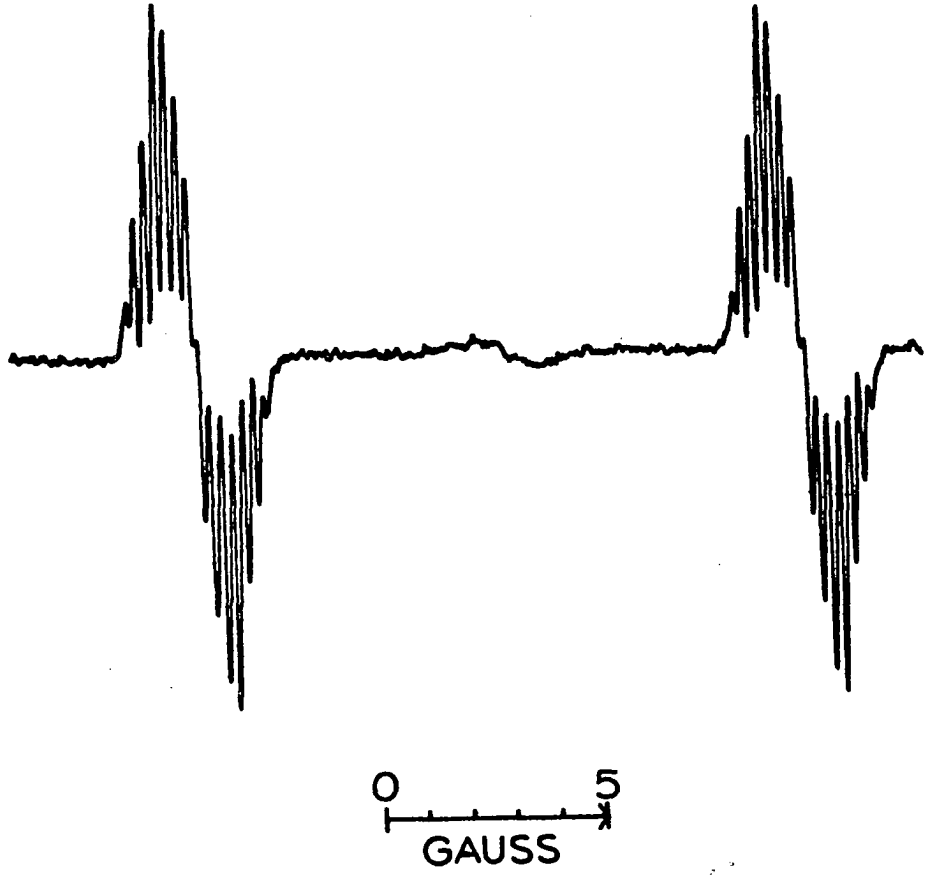


Figure 73. First derivative ESR spectrum of cis-1-methylbicyclo[4.2.0]oct-3-ene-7,8-semidione (XCV) prepared by the reaction of cis-1-methyl-7,8-bis(trimethylsiloxy)bicyclo[4.2.0]octa-3,7-diene (0.1 M) with potassium t-butoxide (0.2 M) in DMSO.

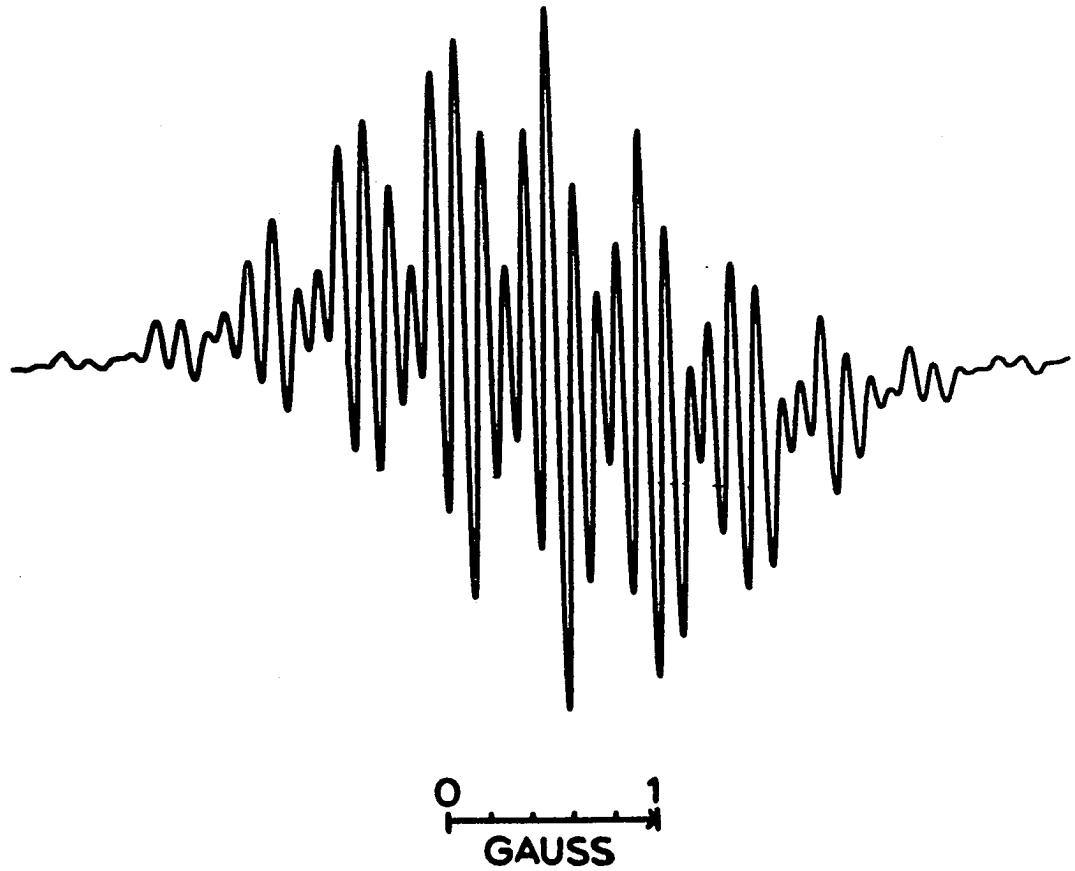


Figure 74. First derivative ESR spectrum of tricyclo[4.4.2.$0^{1,6}$]dodeca-3,8-diene-11,12-semidione (XCIV) prepared by the reaction of 12-hydroxytricyclo-[4.4.2.$0^{1,6}$]dodeca-3,8-dien-11-one (0.05 M) with potassium t-butoxide (0.1 M) in DMSO.

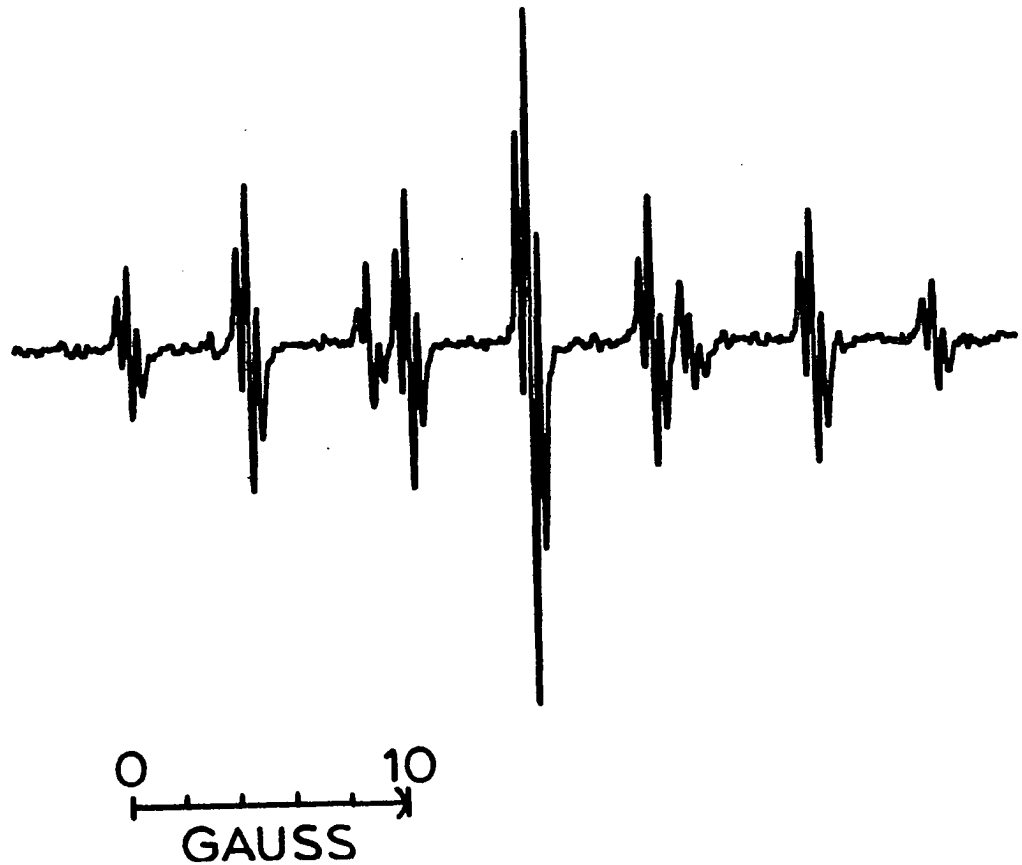


Figure 75. First derivative ESR spectrum of cis-bicyclo[4.2.0]octane-3,4-semidione (XCVI) prepared by the reaction of crude cis-3,4-bis(trimethylsiloxy)-bicyclo[4.2.0]oct-3-ene with potassium t-butoxide in DMSO.

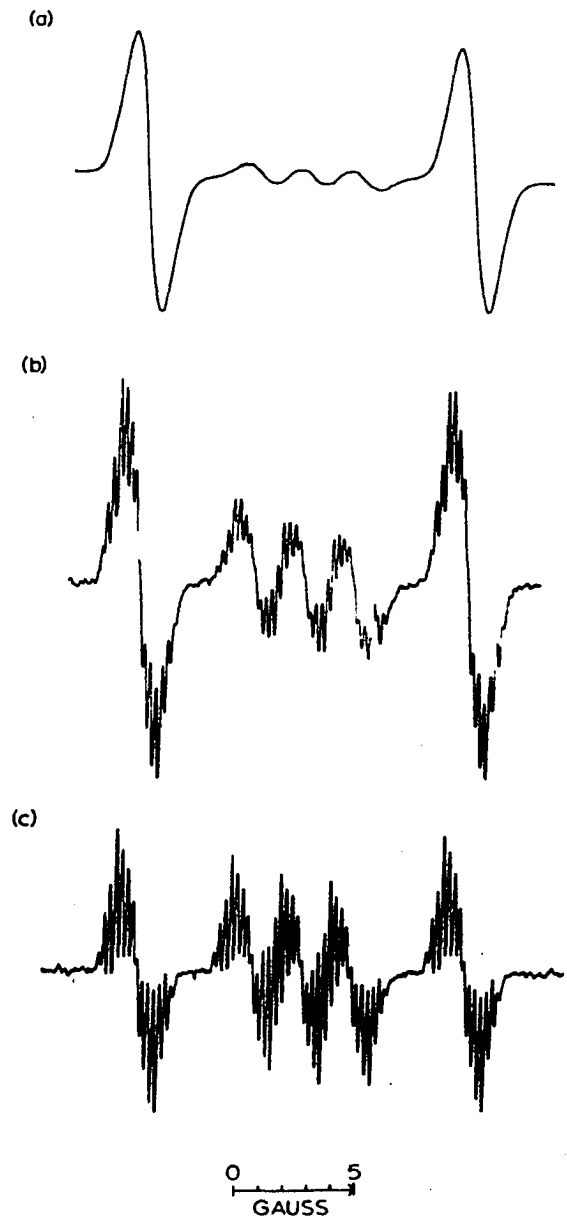


Figure 76. First derivative ESR spectra of the mixture of cis-1-methylbicyclo[4.2.0]oct-3-ene-7,8-semidione and cis-1-methyl-6-deuteriobicyclo[4.2.0]oct-3-ene-7,8-semidione prepared by the reaction of cis-1-methyl-7,8-bis(trimethylsiloxy)bicyclo[4.2.0]octa-3,7-diene (0.1 M) with potassium t-butoxide (0.2 M) in d_6-DMSO; (a) spectrum recorded after 3 minutes; (b) spectrum recorded after 4 hours; (c) spectrum recorded after 7.5 hours.

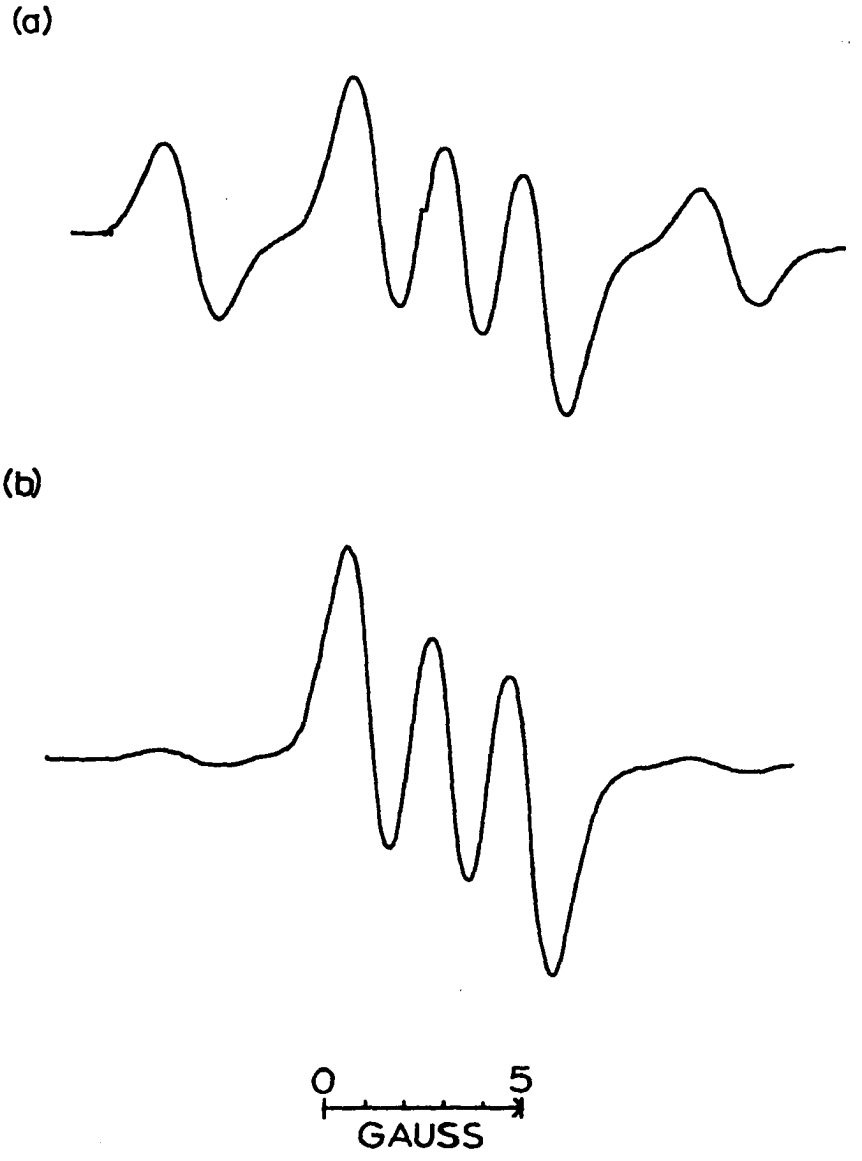


Figure 77. First derivative ESR spectra of the mixture of cis-1-methylbicyclo[4.2.0]oct-3-ene-7,8-semidione and cis-1-methyl-6-deuteriobicyclo[4.2.0]oct-3-ene-7,8-semidione prepared by the reaction of crude trans-1-methyl-7,8-bis(trimethylsiloxy)bicyclo-[4.2.0]octa-3,7-diene with potassium t-butoxide in d_6-DMSO; (a) spectrum recorded after 5 minutes; (b) spectrum recorded after 40 minutes.

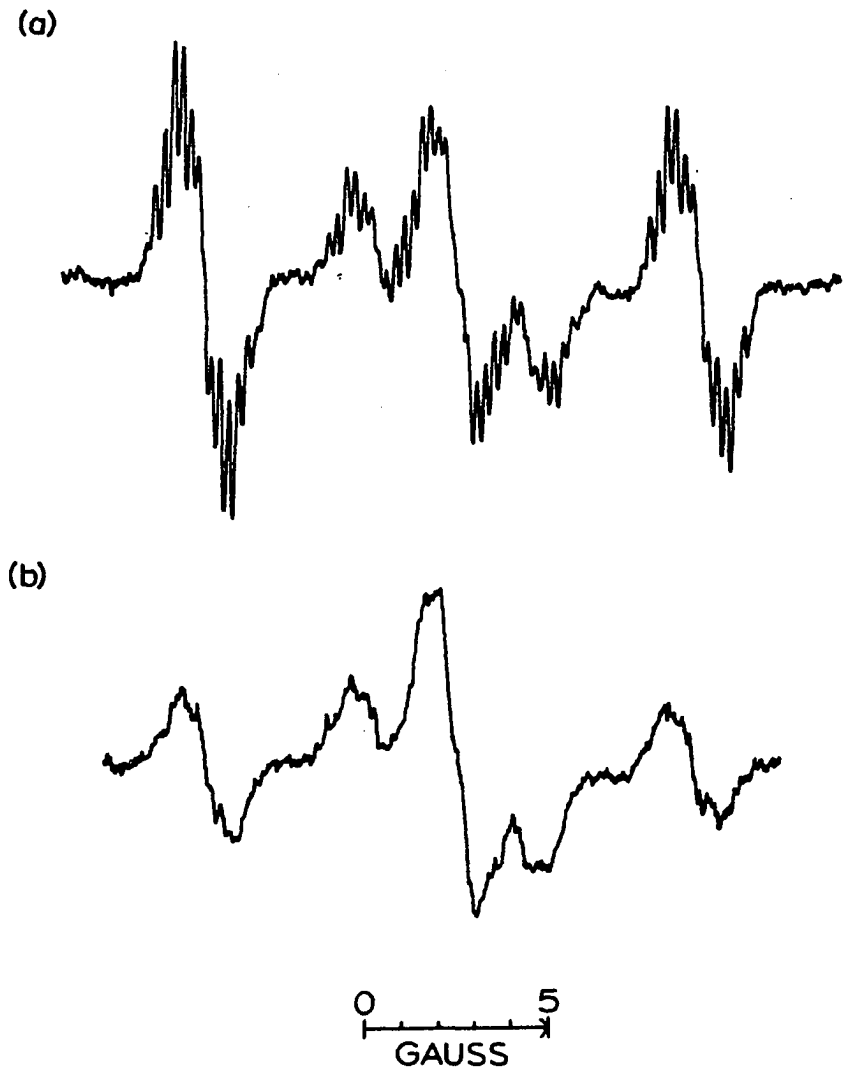


Figure 78. First derivative ESR spectra of the mixture of cis-1-methylbicyclo[4.2.0]oct-3-ene-7,8-semidione and cis-1-methyl-6-deuteriobicyclo[4.2.0]oct-3-ene-7,8-semidione prepared by the reaction of 1-methyl-2,3-bis(trimethylsiloxy)-1,3,6-cyclooctatriene (0.1 M) with potassium t-butoxide (0.2 M) in d_6-DMSO; (a) spectrum recorded after 25 minutes; (b) spectrum recorded after 45 minutes.

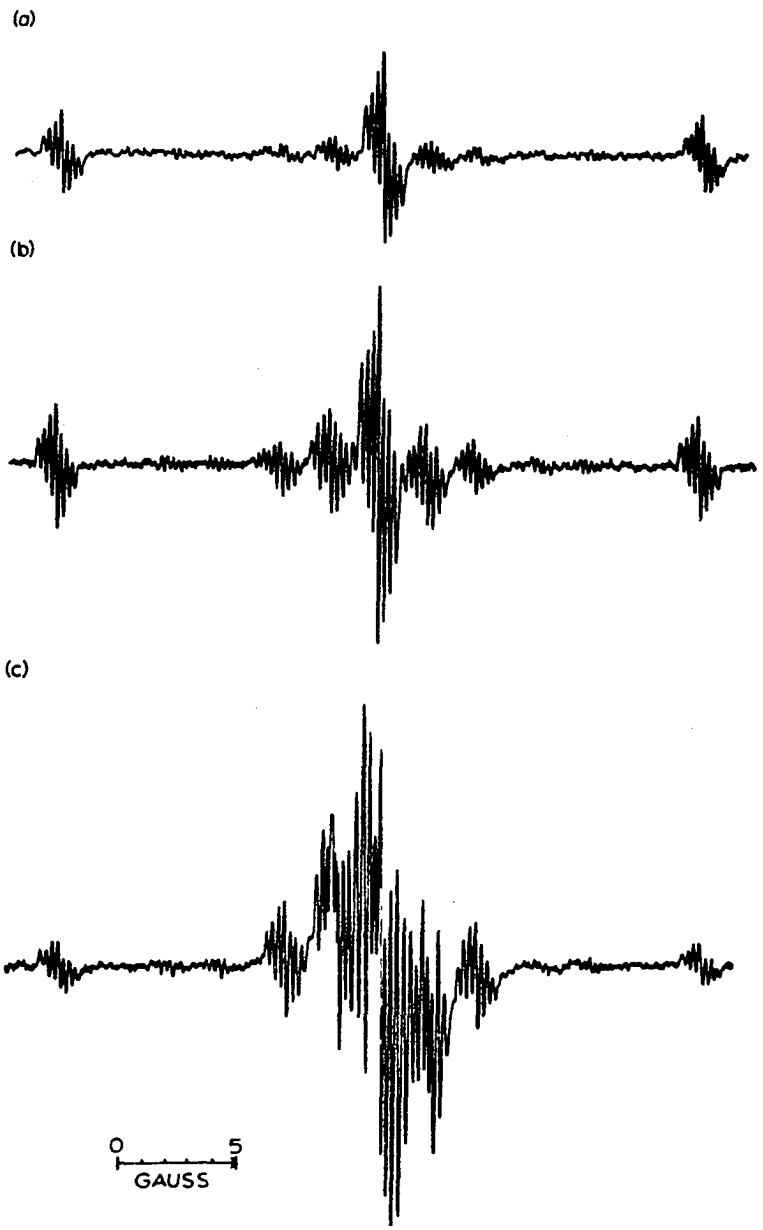


Figure 79. First derivative ESR spectra of the mixture of cis-bicyclo[4.2.0]octane-7,8-semidione, cis-1-deuteriobicyclo[4.2.0]octane-7,8-semidione and cis-1,6-dideuteriobicyclo[4.2.0]octane-7,8-semidione prepared by the reaction of cis-7,8-bis-(trimethylsiloxy)bicyclo[4.2.0]oct-7-ene (0.1 M) with potassium t-butoxide (0.2 M) in d_6-DMSO; (a) spectrum recorded after 30 minutes; (b) spectrum recorded after 60 minutes; (c) spectrum recorded after 150 minutes.

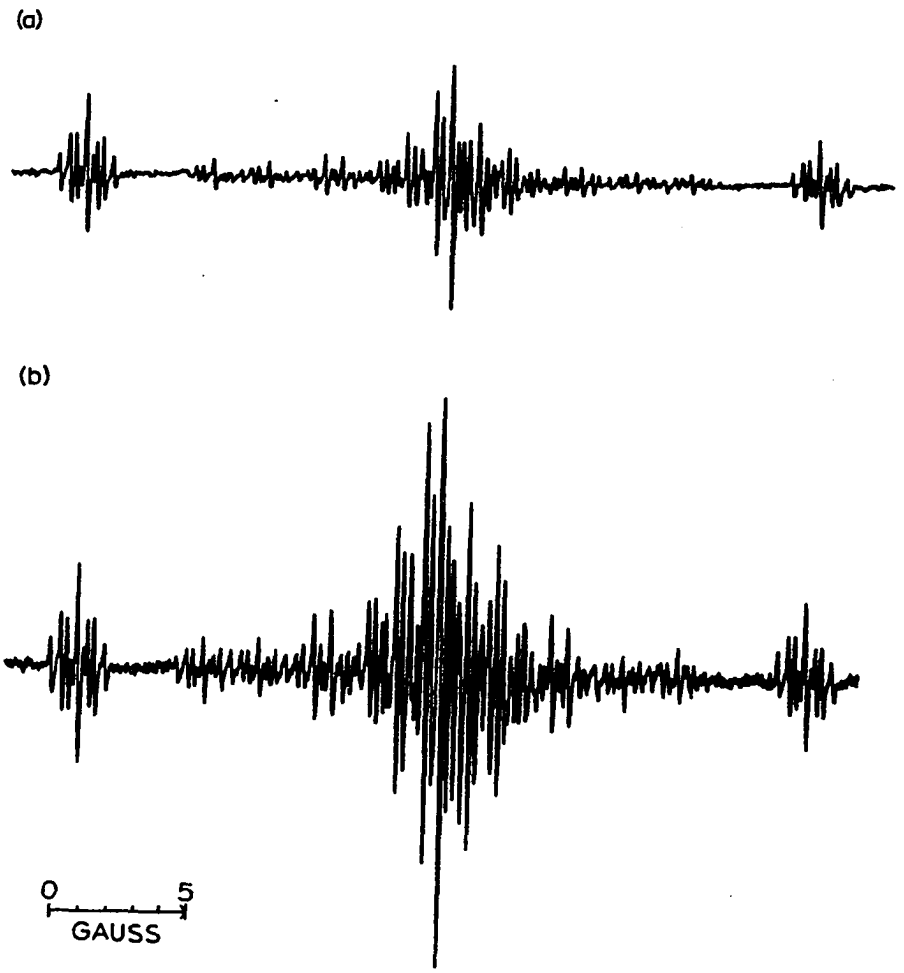


Figure 80. First derivative ESR spectra of the mixture of cis-bicyclo[4.2.0]oct-3-ene-7,8-semidione, cis-1-deuteriobicyclo[4.2.0]oct-3-ene-7,8-semidione and cis-1,6-dideuteriobicyclo[4.2.0]oct-3-ene-7,8-semidione prepared by the reaction of cis-7,8-bis(trimethylsiloxy)bicyclo[4.2.0]octa-3,7-diene (0.1 M) with potassium t-butoxide (0.2 M) in d_6-DMSO; (a) spectrum recorded after 7.5 hours; (b) spectrum recorded after 23 hours.

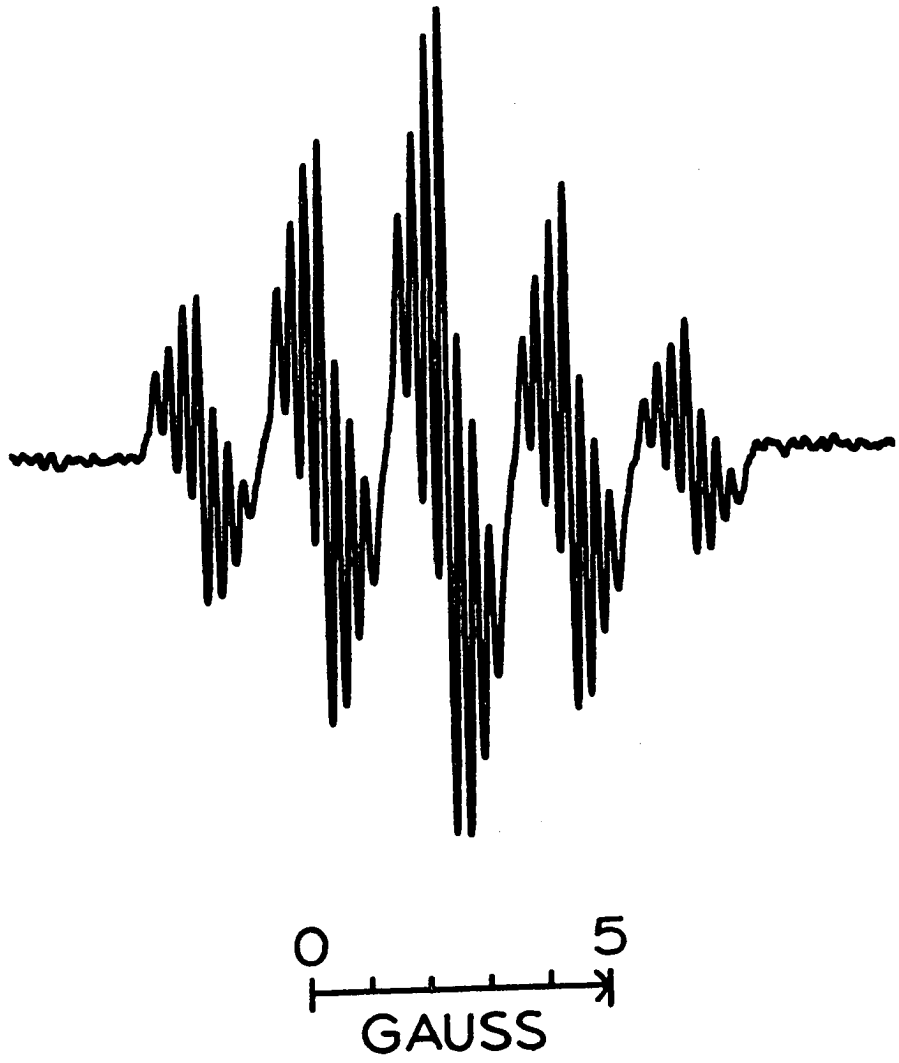


Figure 81. First derivative ESR spectrum of cis-1,6-dideuteriobicyclo[4.2.0]octane-7,8-semidione prepared by the reaction of cis-7,8-bis(trimethylsiloxy)bicyclo[4.2.0]oct-7-ene (0.1 M) with potassium t-butoxide (0.2 M) in d_6-DMSO containing 5% (by volume) deuterium oxide (spectrum recorded after 5 minutes).

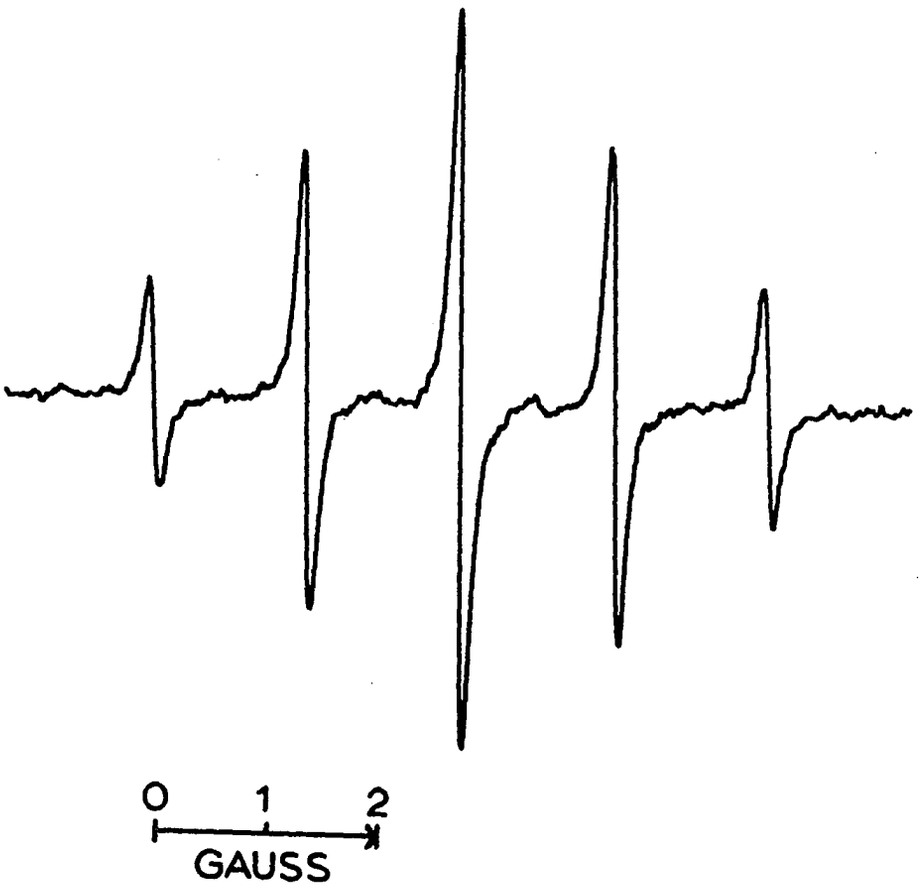


Figure 82. First derivative ESR spectrum of the semidione (XCIX) derived from the reduction of di-t-butyl-1,2-diazetidinedione in DME with sodium-potassium alloy.

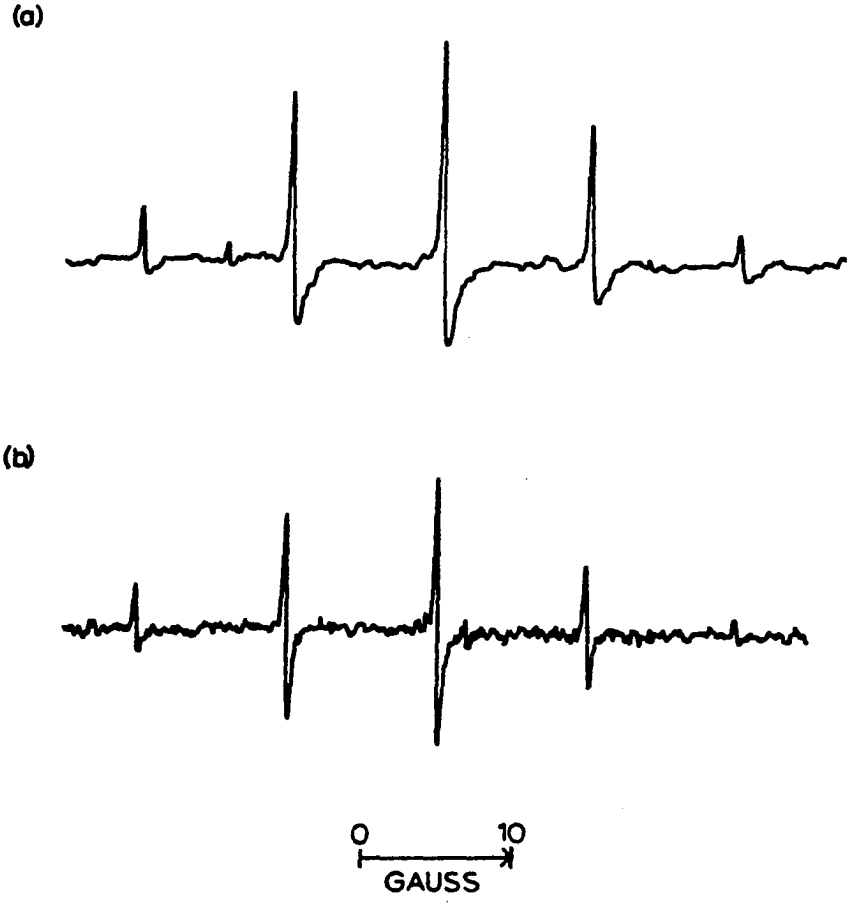


Figure 83. First derivative ESR spectra of the semidione formed when: (a) dimethyl cis-1,2-cyclobutane-dicarboxylate was reacted with sodium-potassium alloy in DME; (b) dimethyl cis-1,2-cyclobutane-dicarboxylate was reacted with sodium-potassium alloy in ether at 0° in the presence of chloro-trimethylsilane and this crude product was reacted with potassium t-butoxide in DMSO.

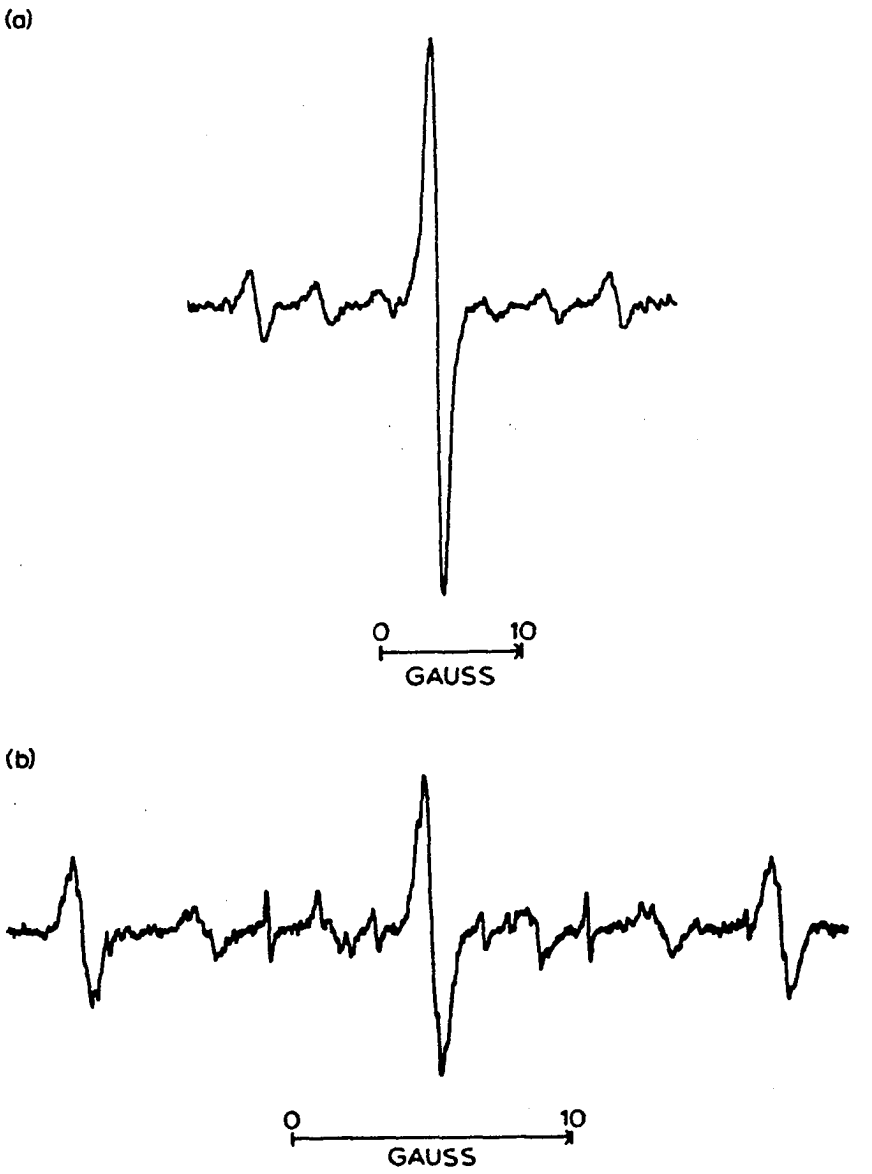


Figure 84. First derivative ESR spectra of the semidiones formed when: (a) dimethyl cis-7,8-dimethylbicyclo-[4.2.0]octane-7,8-dicarboxylate was reacted with sodium-potassium alloy in DME; (b) dimethyl cis-7,8-dimethylbicyclo[4.2.0]octane-7,8-dicarboxylate was reacted with sodium-potassium alloy in ether at 0° in the presence of chlorotrimethylsilane and this crude product was reacted with potassium t-butoxide in DMSO.

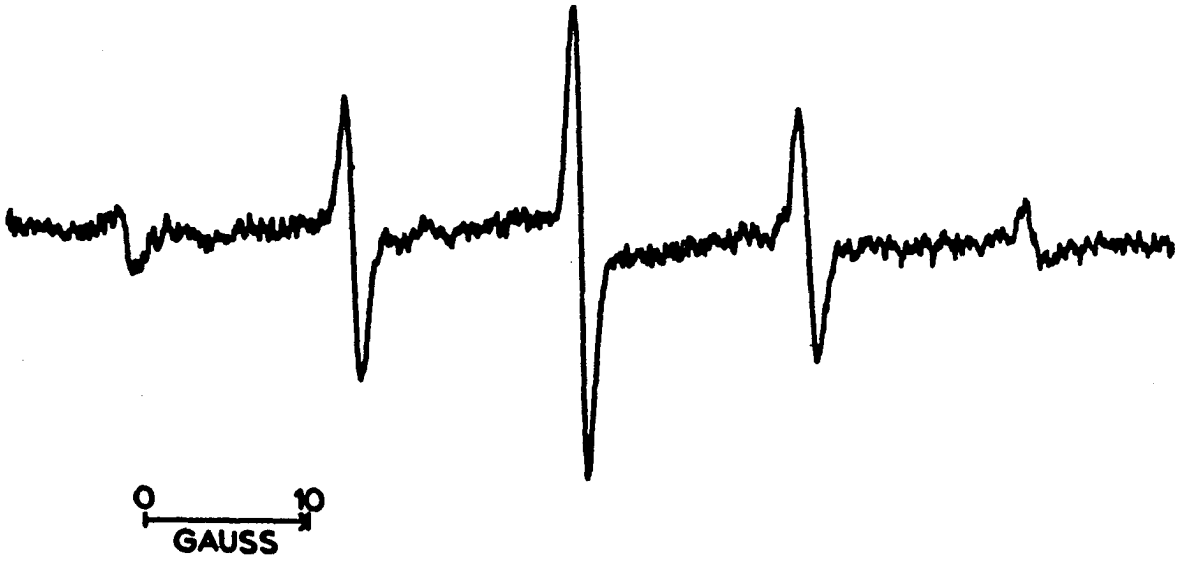


Figure 85. First derivative ESR spectrum of the semidione formed when dimethyl cis-1,2-cyclopropanedicarboxylate was reacted with sodium-potassium alloy in DME.

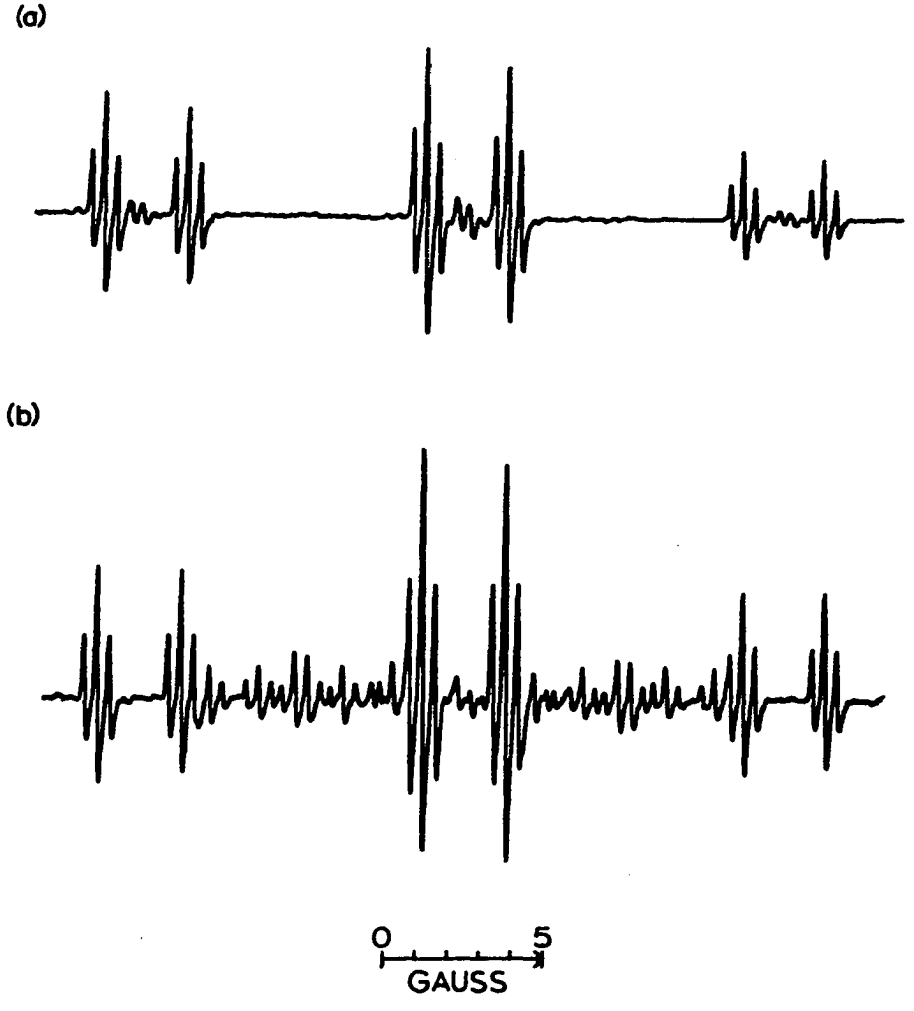


Figure 86. First derivative ESR spectra of the semidiones formed when 1,5-dicarbomethoxytetracyclo-[3.2.0.$0^{2,7}$.$0^{4,6}$]heptane was reacted with sodium-potassium alloy in ether at 0° in the presence of chlorotrimethylsilane, and this crude product was reacted with potassium t-butoxide in: (a) DMSO; (b) d_6-DMSO.

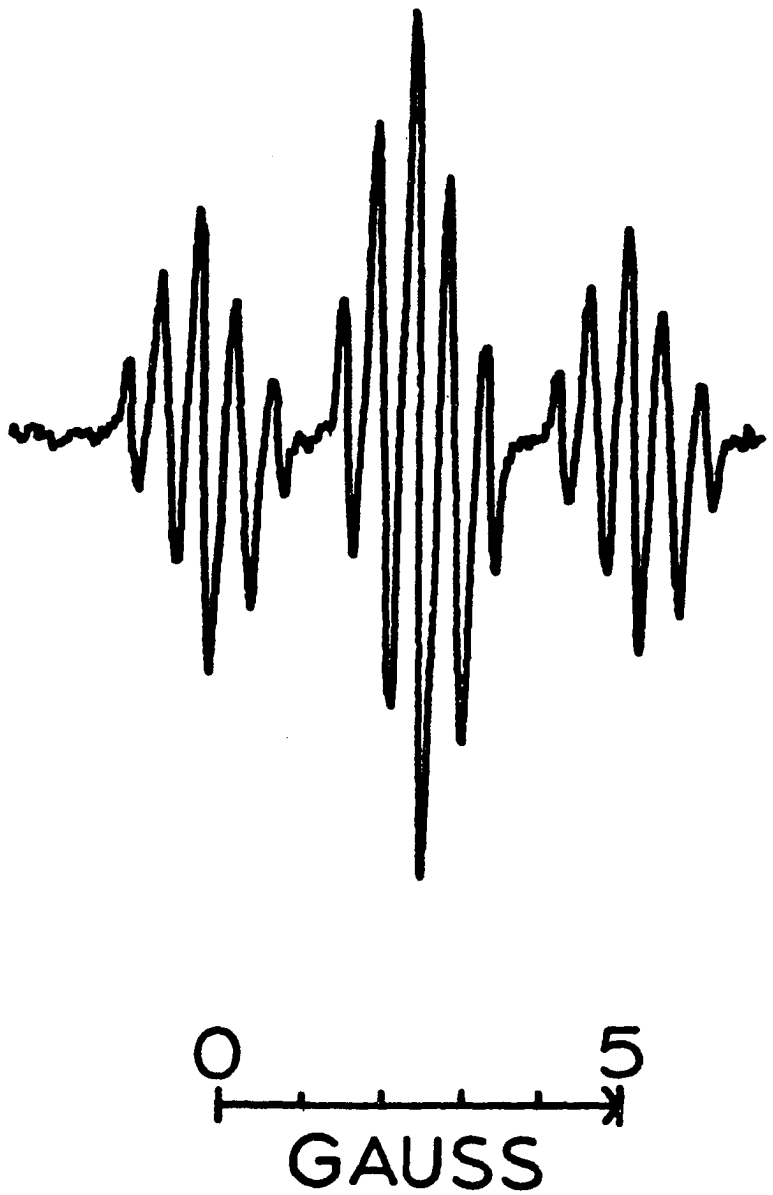


Figure 87. First derivative ESR spectrum of the radical anion formed when 1,5-dicarbomethoxy-3-oxo-tetracyclo-[3.2.0.$0^{2,7}$.$0^{4,6}$]heptane was reacted with sodium-potassium alloy in ether at 0° in the presence of chlorotrimethylsilane, and this crude product was reacted with potassium t-butoxide in DMSO.

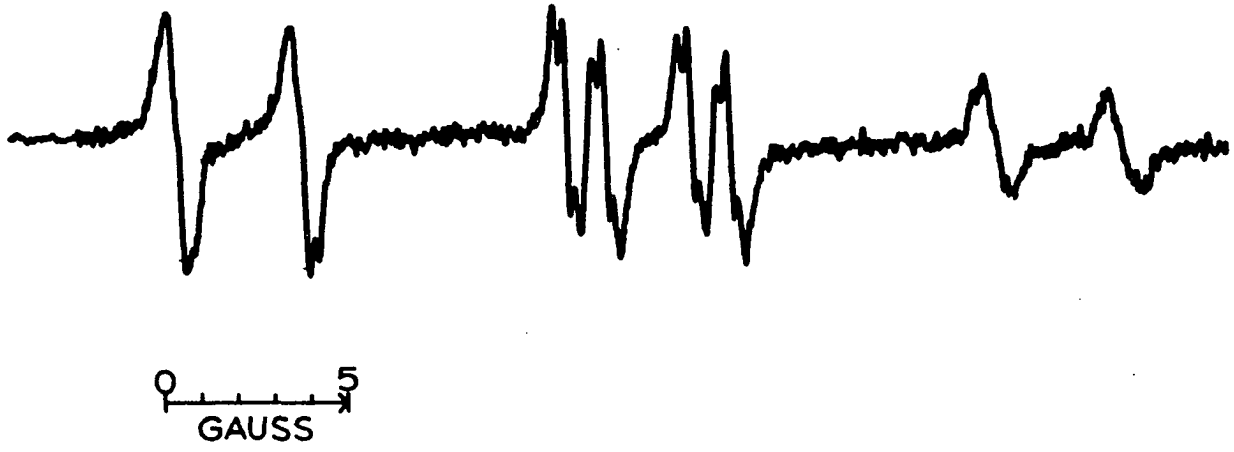


Figure 88. First derivative ESR spectrum of tricyclo[3.2.0.$0^{4,6}$]heptane-2,3-semidione (CXII) prepared by the <u>in situ</u> acyloin condensation of dimethyl-bicyclo[2.1.0]pentane-<u>endo</u>, <u>endo</u>-2,5-dicarboxylate with sodium-potassium alloy in DME.

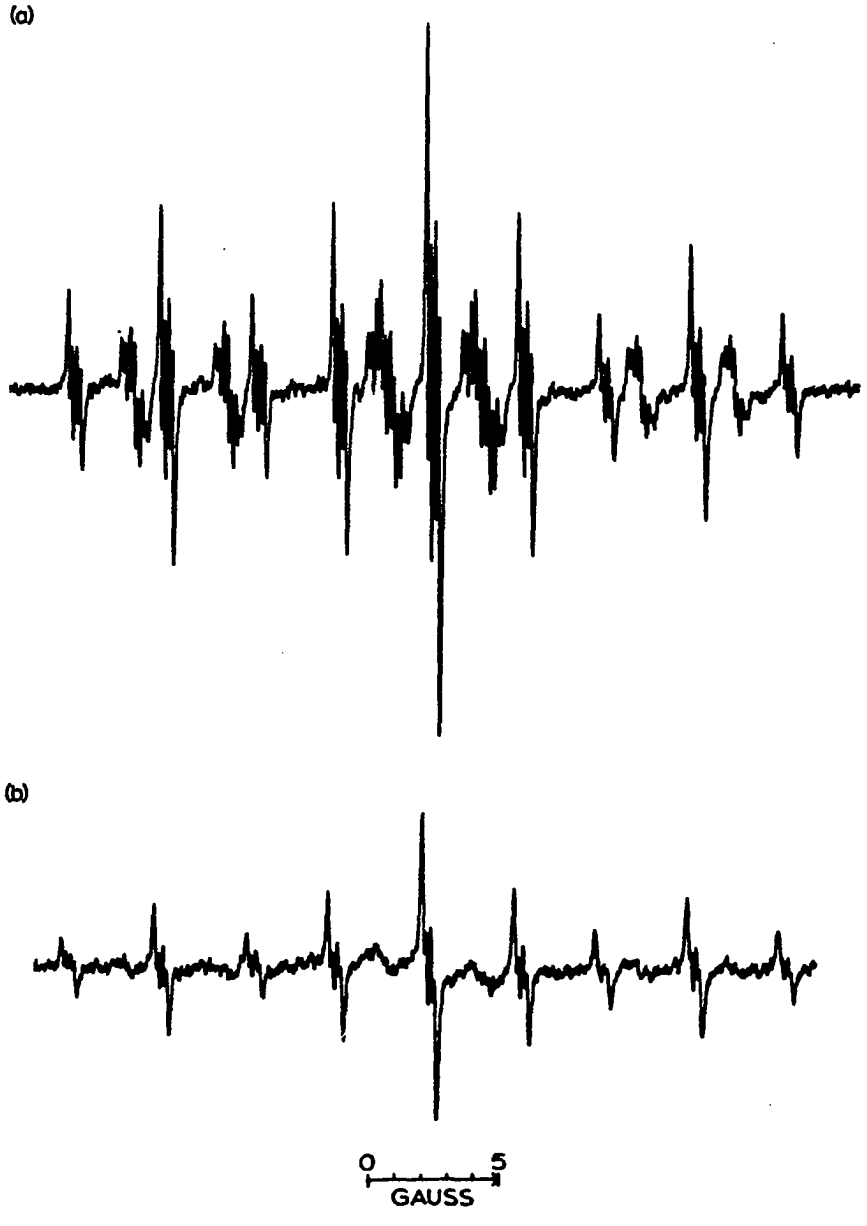


Figure 89. First derivative ESR spectra of the mixture of semidiones produced by the reaction of dimethyl bicyclo[2.1.0]pentane-endo, endo-2,5-dicarboxylate with sodium-potassium alloy in ether at 0° in the presence of chlorotrimethylsilane, followed by reaction of this crude product with potassium t-butoxide in DMSO; (a) spectrum recorded after 15 minutes; (b) spectrum recorded after 2 hours.

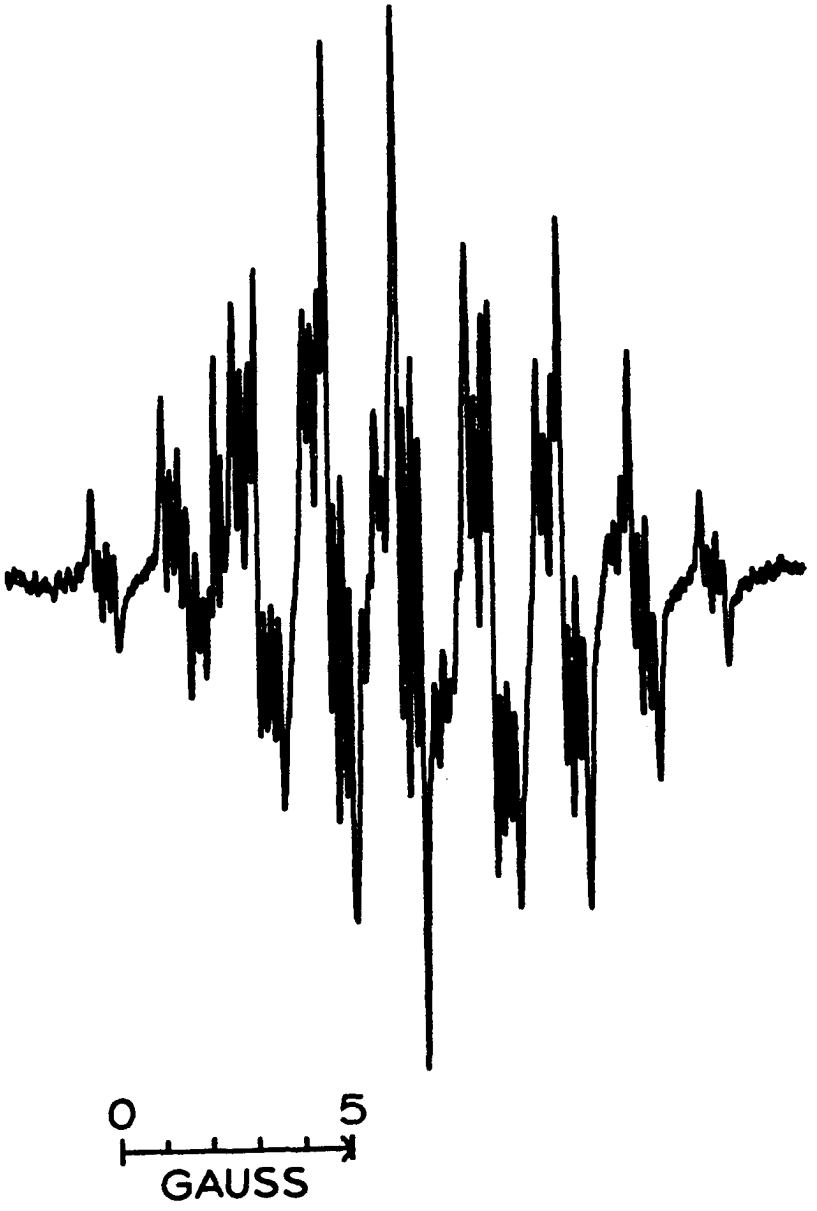


Figure 90. First derivative ESR spectrum of the semidione formed when dimethyl bicyclo[2.1.0]pentane-endo, endo-2,5-dicarboxylate was reacted with sodium-potassium alloy in ether at 0° in the presence of chlorotrimethylsilane, followed by reaction of this crude product with potassium t-butoxide in d_6-DMSO.

Figure 91. First derivative ESR spectrum of tricyclo-[2.2.2.$0^{2,6}$]octane-7,8-semidione (CXIV) prepared by the reduction of tricyclo[2.2.2.$0^{2,6}$]octan-7,8-dione (0.05 M) in DMSO containing propiophenone (0.02 M) and potassium t-butoxide (0.1 M).

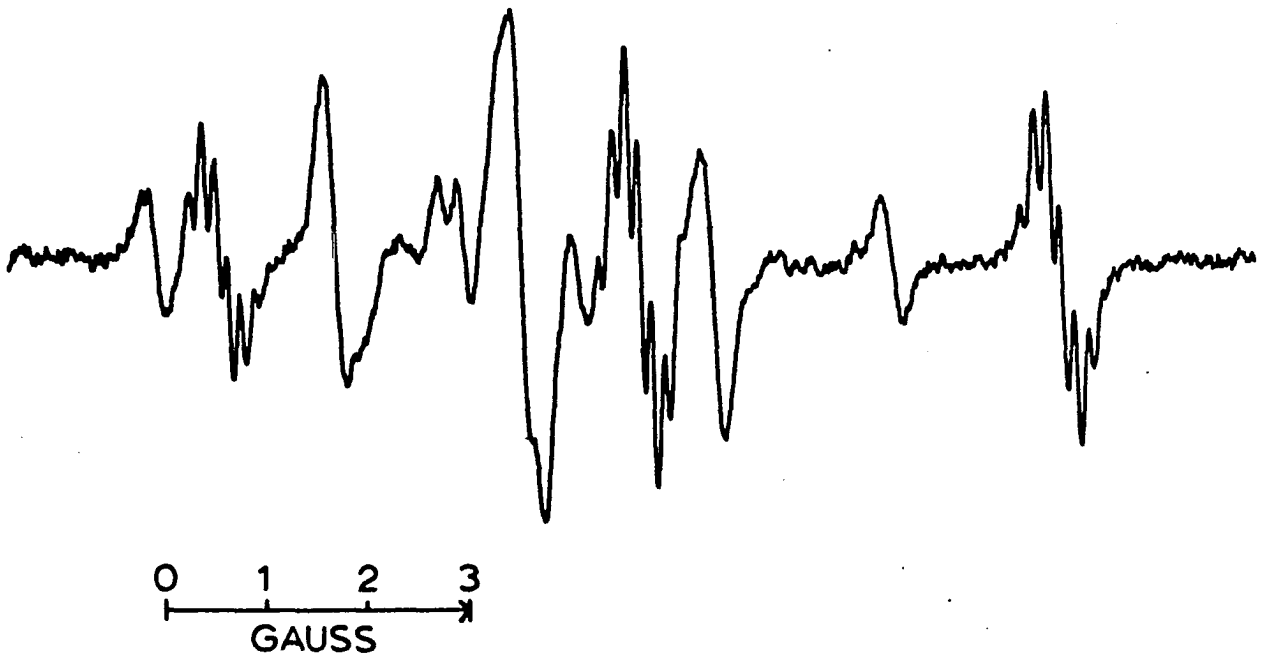


Figure 92. First derivative ESR spectrum of the mixture of radical anions produced when dimethyl bicyclo[3.1.0]hexane-endo-3-syn-6-dicarboxylate was reacted with sodium-potassium alloy in ether at 0° in the presence of chlorotrimethylsilane, followed by reaction of this crude product with potassium t-butoxide in DMSO (spectrum recorded after 1 hour).

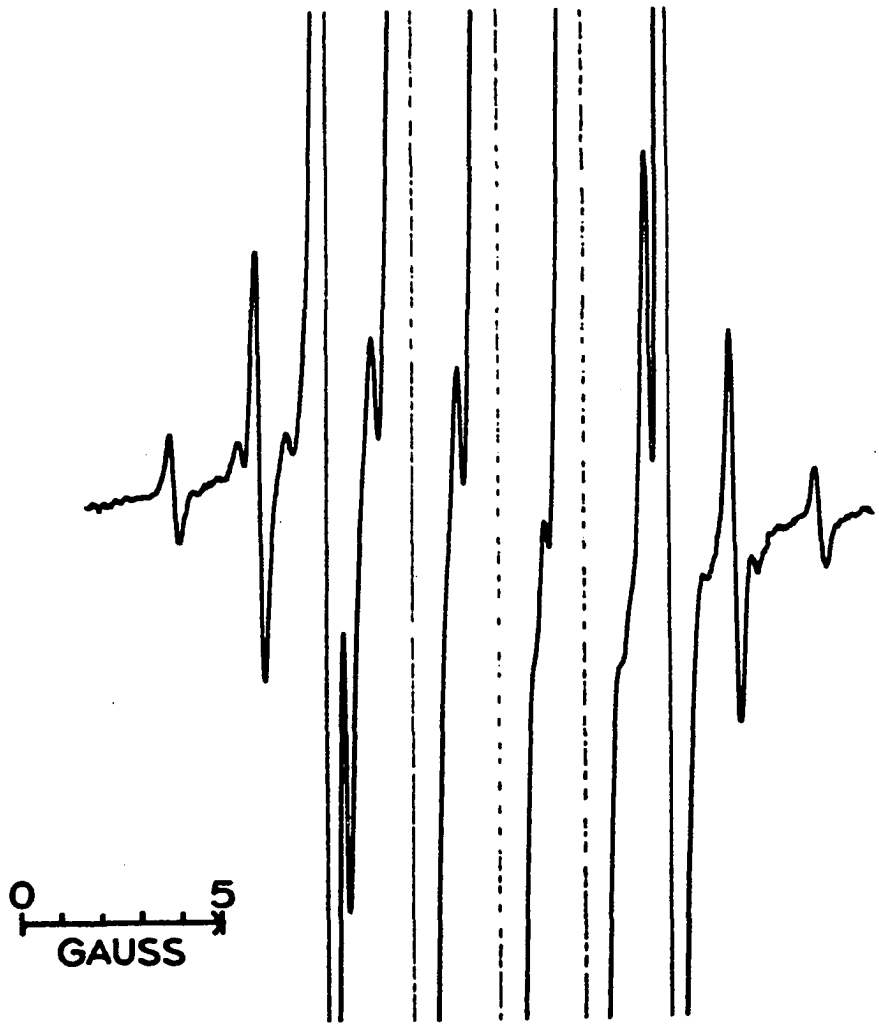


Figure 93. First derivative ESR spectrum of bicyclo[2.2.2]-octane-2,3-semidione prepared by the *in situ* acyloin condensation of dimethyl *cis*-1,4-cyclohexanedicarboxylate with sodium-potassium alloy in DME (spectrum amplitude sufficiently high to reveal natural abundance carbon-13 couplings).

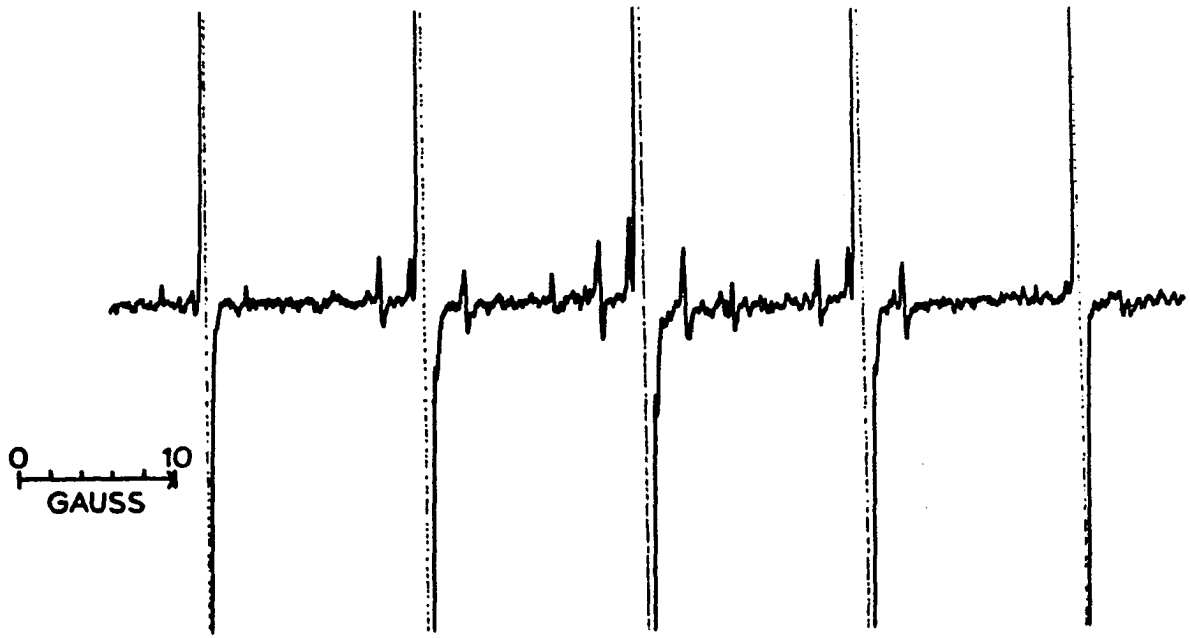


Figure 94. First derivative ESR spectrum of cyclobutanesemidione (LXI) prepared by the reaction of 1,2-bis(trimethylsiloxy)cyclobutene (0.1 M) with potassium t-butoxide (0.2 M) in DMSO (spectrum amplitude sufficiently high to reveal natural abundance carbon-13 couplings).

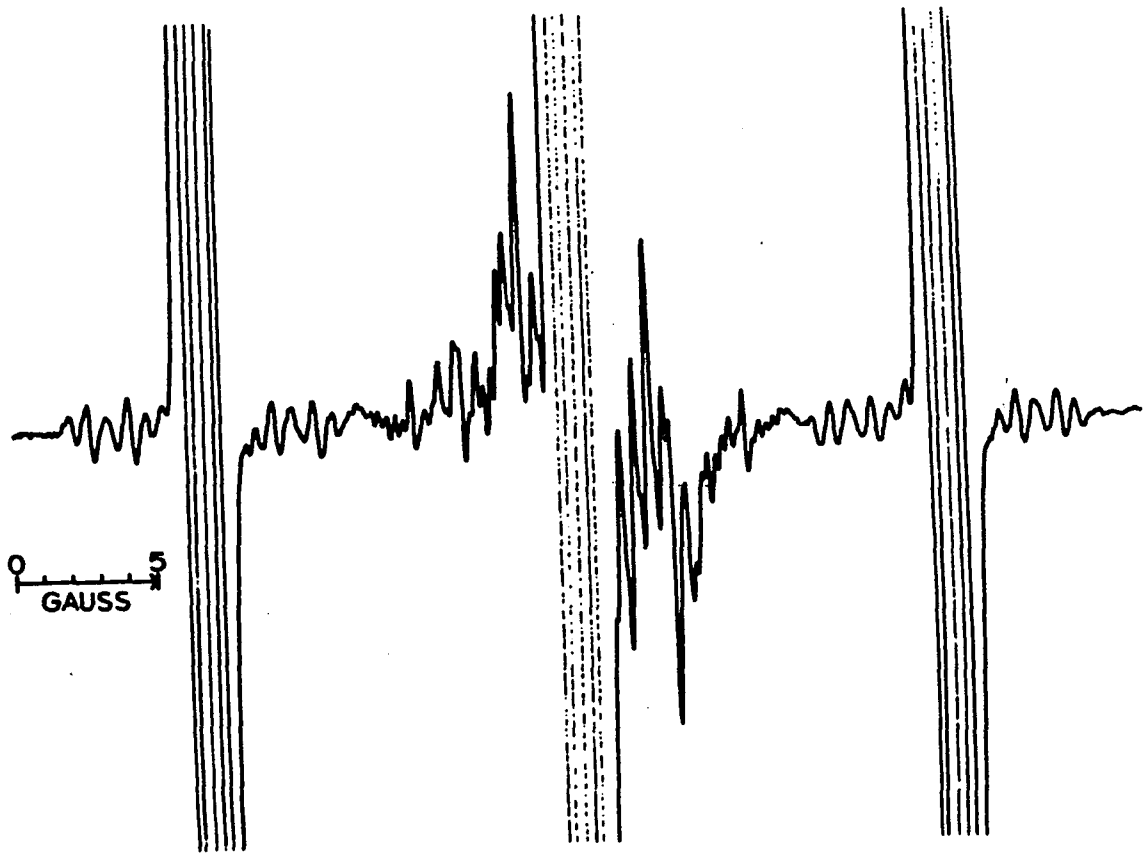


Figure 95. First derivative ESR spectrum of cis-3,4-dimethyl bicyclo[4.2.0]oct-3-ene-7,8-semidione (XCIII) prepared by the reaction of cis-3,4-dimethyl-7,8-bis(trimethylsiloxy)bicyclo[4.2.0]octa-3,7-diene (0.1 M) with potassium t-butoxide (0.2 M) in DMSO (spectrum amplitude sufficiently high to reveal natural abundance carbon-13 couplings).

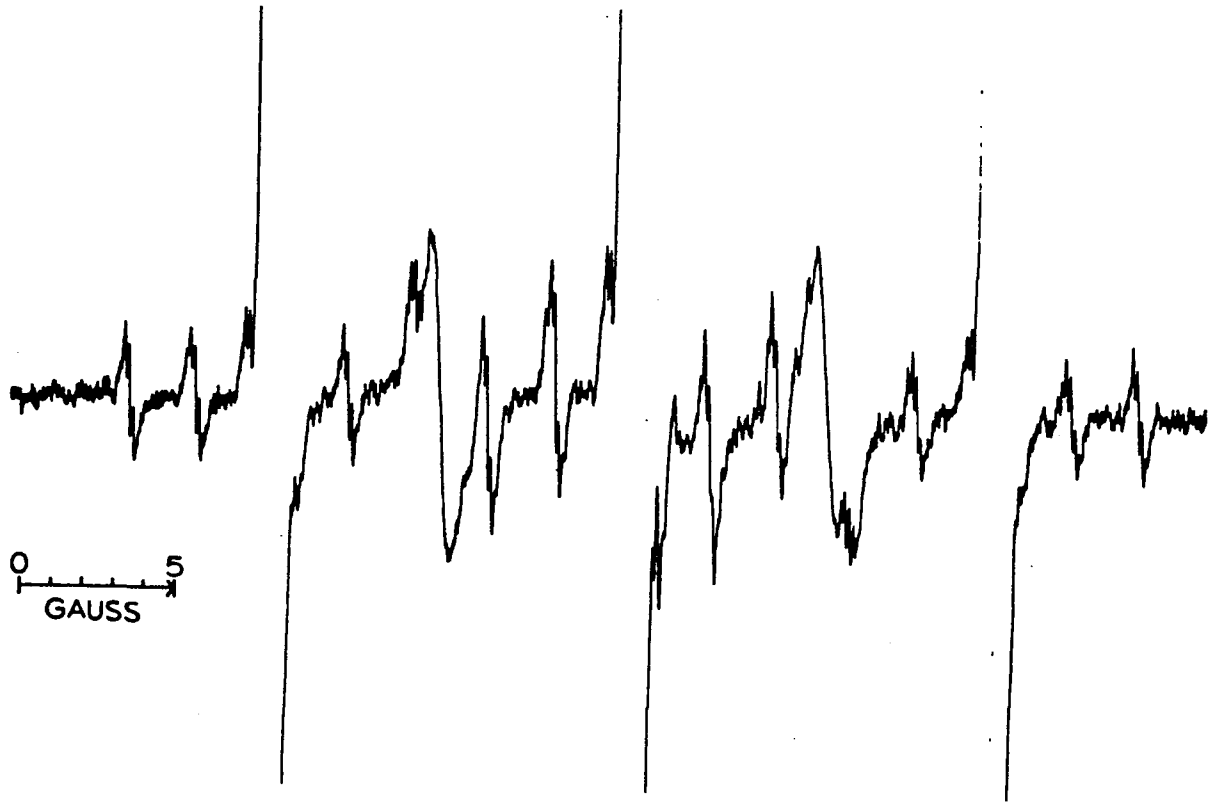


Figure 96. First derivative ESR spectrum of endo-hexacyclo[4.4.2.$0^{2,5}$.$0^{7,10}$.$0^{9,11}$.$0^{8,12}$]dodecane-3,4-semidione (LXVII) prepared by reaction of the corresponding crude bis(trimethylsiloxy)alkene with potassium t-butoxide in DMSO (spectrum amplitude sufficiently high to reveal natural abundance carbon-13 couplings).

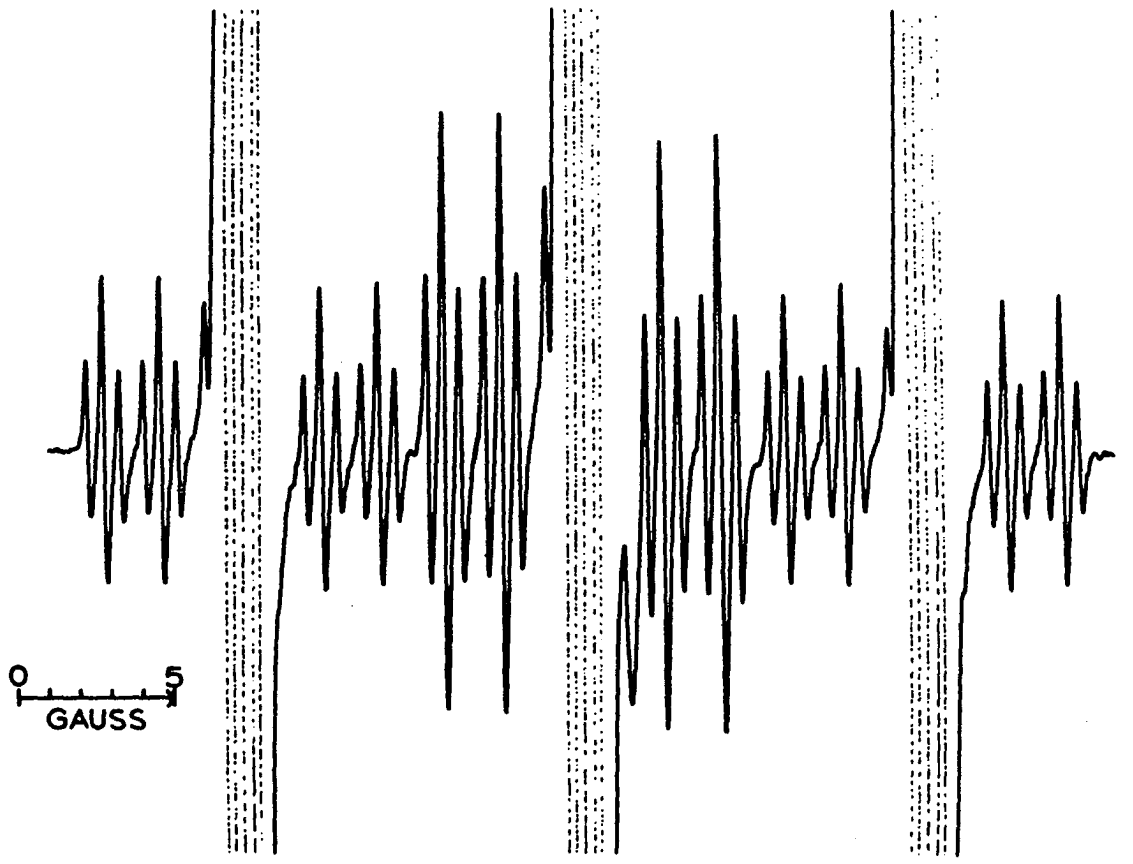


Figure 97. First derivative ESR spectrum of 7,8; 9,10-dibenzotricyclo[4.2.2.$0^{2,5}$]-deca-7,9-diene-3,4-semidione (LXVIII) prepared by reaction of the corresponding crude bis(trimethylsiloxy)alkene with potassium t-butoxide in DMSO (spectrum amplitude sufficiently high to reveal natural abundance carbon-13 couplings).

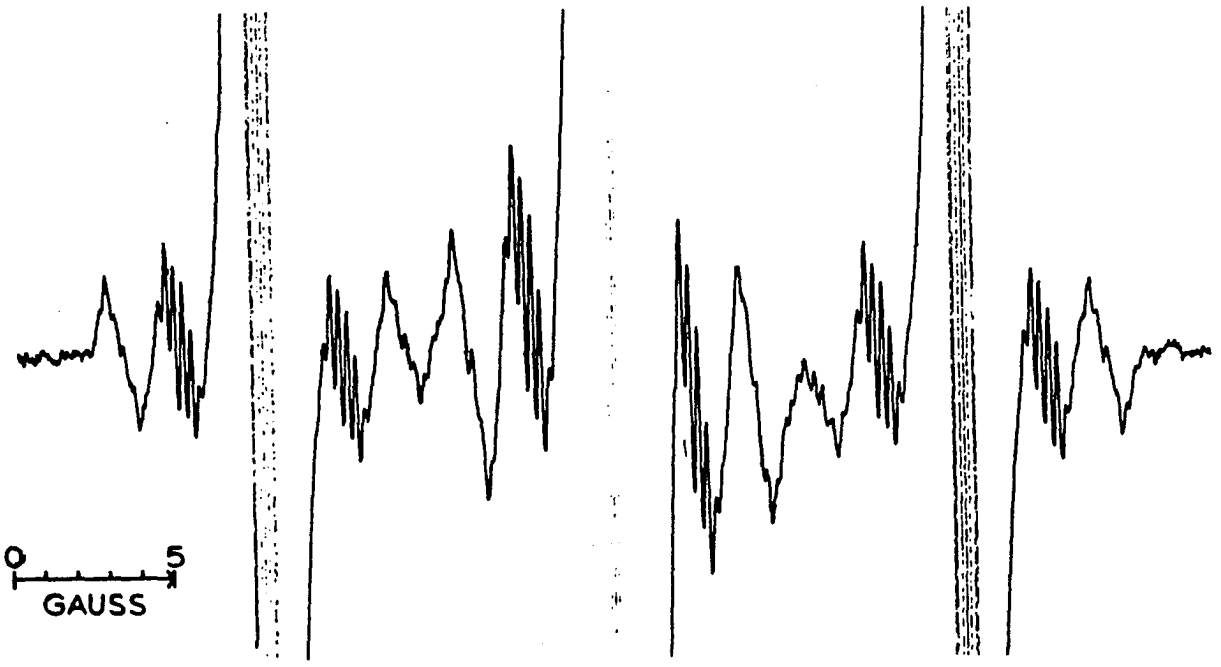


Figure 98. First derivative ESR spectrum of 1-methyl-7,8;9,10-dibenzotricyclo-[4.2.2.$0^{2,5}$]deca-7,9-diene-3,4-semidione (LXX) prepared by reaction of the corresponding crude bis(trimethylsiloxy)alkene with potassium t-butoxide in DMSO (spectrum amplitude sufficiently high to reveal natural abundance carbon-13 couplings).

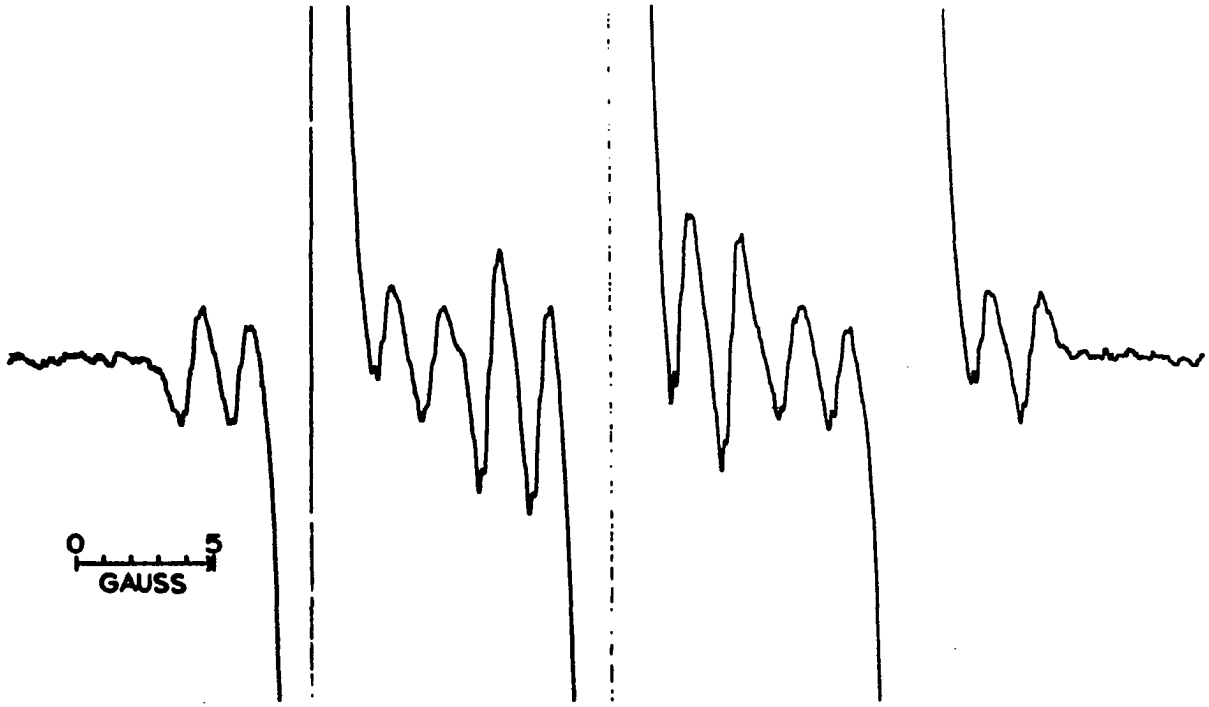


Figure 99. First derivative ESR spectrum of 1,6-dimethyl-7,8;9,10-dibenzotricyclo-[4.2.2.$0^{2,5}$]deca-7,9-diene-3,4-semidione (LXXI) prepared by reaction of the corresponding crude bis(trimethylsiloxy)alkene with potassium t-butoxide in DMSO (spectrum amplitude sufficiently high to reveal natural abundance carbon-13 couplings).

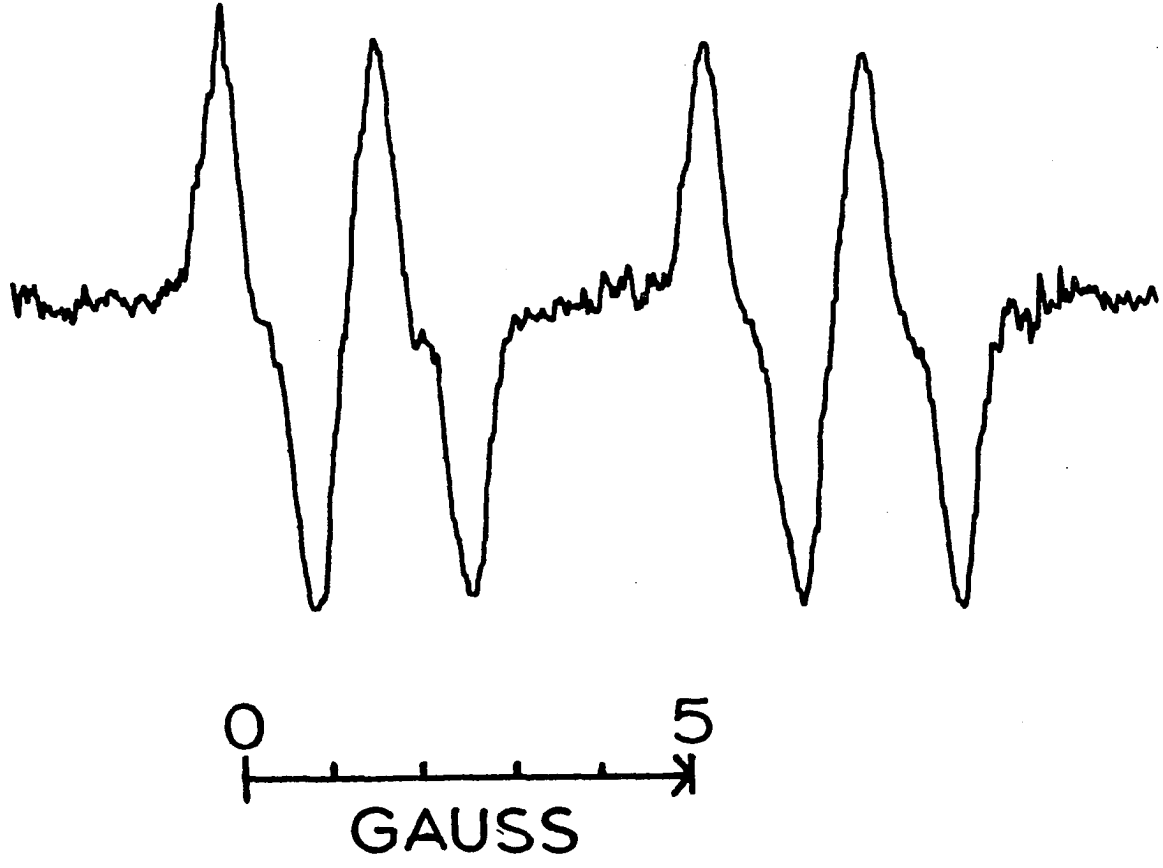


Figure 100. First derivative ESR spectrum of semidione CXX prepared by the oxidation of 9β,10β-dimethyl-7α-isopropyl-3-octal-2-one (0.1 M) in DMSO containing potassium t-butoxide (0.2 M).

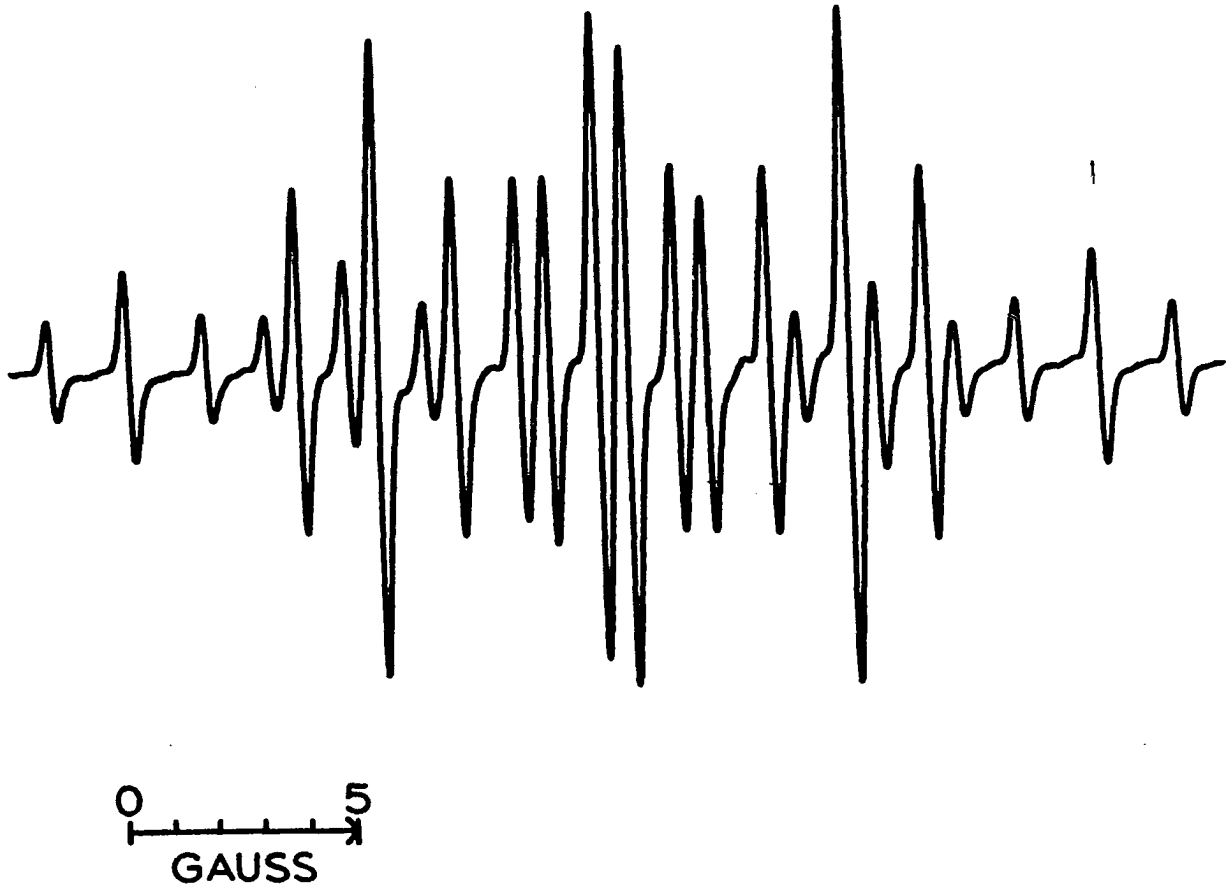


Figure 101. First derivative ESR spectrum of radical anion CXXI prepared by the oxidation of isophorone (0.1 M) in DMSO containing potassium t-butoxide (0.2 M).

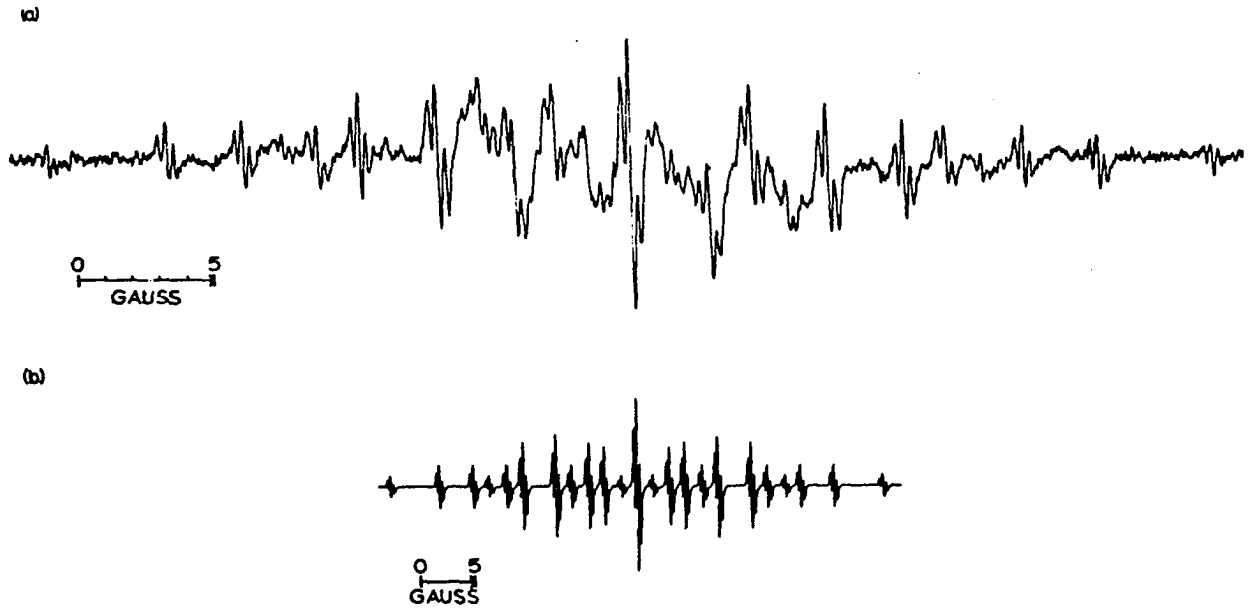


Figure 102. (a) First derivative ESR spectrum of the radical anions obtained from the oxidation of 4,5,6,7-tetrahydroindan-1-one (0.1 M) in DMSO containing potassium t-butoxide (0.2 M); (b) simulated spectrum with a Lorentzian linewidth of 0.20 gauss and hfsc from text performed by JEOLCO JNM-RA-1 spectrum accumulator.

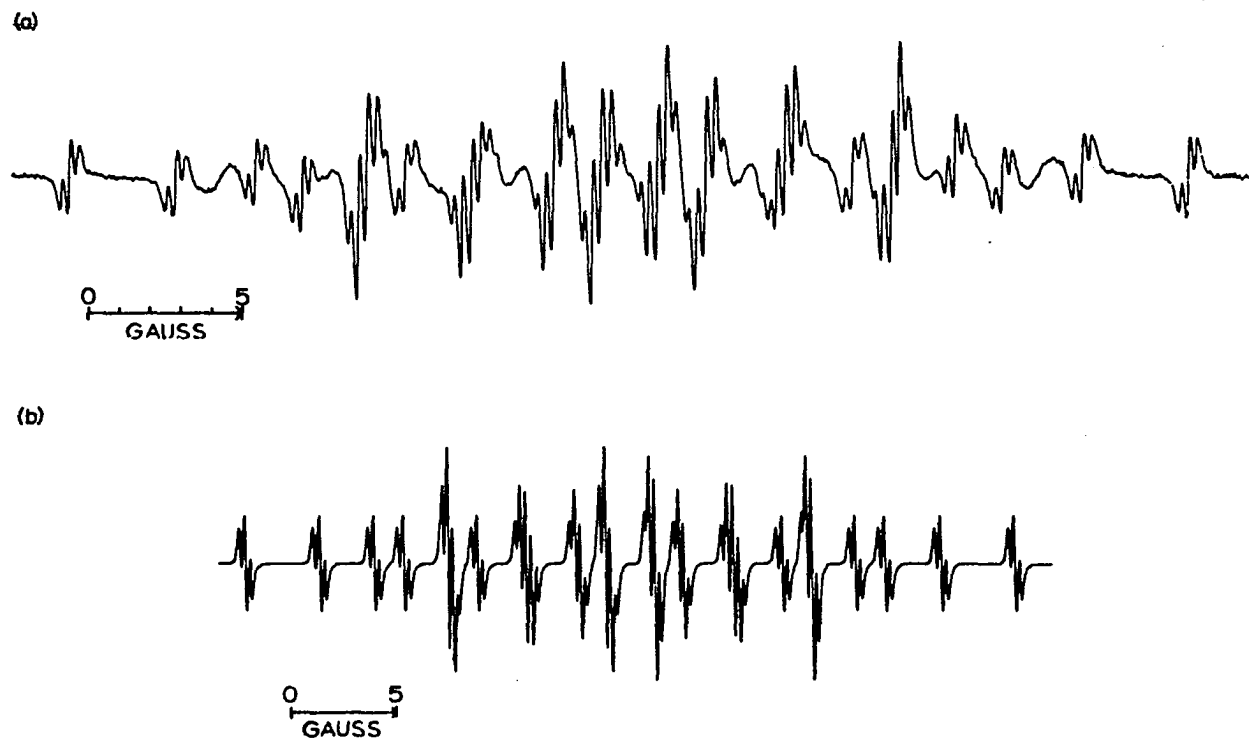


Figure 103 (a) First derivative ESR spectrum of the radical anions obtained from the oxidation of 3-methyl-4,5,6,7-tetrahydroindan-1-one (0.1 M) in DMF containing potassium t-butoxide (0.3 M); (b) simulated spectrum with a Lorentzian linewidth of 0.30 gauss and hfsc from text performed by JEOLCO JNM-RA-1 spectrum accumulator.

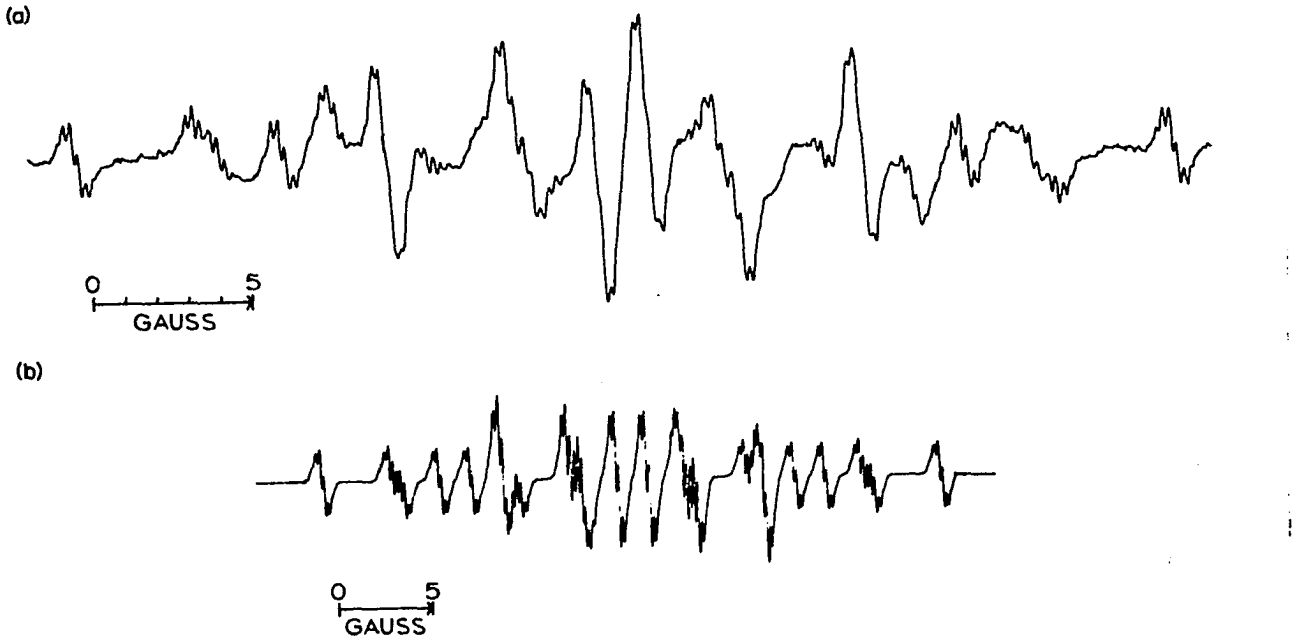


Figure 104. (a) First derivative ESR spectrum of the radical anions obtained from the oxidation of 2-methyl-4,5,6,7-tetrahydroindan-1-one (0.1 M) in DMSO containing potassium t-butoxide (0.3 M); (b) simulated spectrum with a Lorentzian linewidth of 0.30 gauss and hfsc from text performed by JEOLCO JNM-RA-1 spectrum accumulator.

EXPERIMENTAL

Preparation of Reagents

The general reagents employed were commercially available products. Solvents were used as received or, if high purity was important, were distilled from suitable desiccants and stored over molecular sieves in glass stoppered bottles. Dimethyl sulfoxide was distilled at reduced pressure from calcium hydride and stored over molecular sieves. Commercial potassium t-butoxide was sublimed (140°C at 0.1 mm) and stored in a desiccator. Sodium-potassium alloy was prepared by stirring the pure metals (in the desired ratio by weight) in refluxing DME and was stored under dry DME (distilled from sodium-potassium alloy).

cis-1,3-Dicarbomethoxy-1,2,2-trimethylcyclopentane

Diazomethane (from 9.0 g Diazald) in 60 ml ether was distilled into a solution of 2.0 g d-camphoric acid in 50 ml ether at 0°. After 4 hours at 0°, acetic acid was added dropwise to decompose the excess diazomethane, the ethereal solution was extracted with 10% sodium hydroxide (2 x 10 ml) and saturated sodium chloride solution (2 x 15 ml) and dried over magnesium sulfate. Evaporation of the ether left essentially pure diester (56).

NMR (CCl_4) δ0.71 (s, 3H), δ1.17 (s, 3H), δ1.20 (s, 3H), δ1.2-2.9 (complex multiplet, 5H), δ3.60 (s, 6H).

1,2-Bis(trimethylsiloxy)cyclobutene (LXIa)

To a suspension of finely divided sodium (3.5 g, 0.15 mole) in 50 ml of refluxing toluene (under nitrogen) was added 12 ml of chlorotrimethylsilane. A solution of 4.5 g (0.026 mole) of diethyl succinate in 20 ml of toluene was added over a period of one hour. After refluxing an additional four hours, the mixture was cooled and filtered. The solvent was removed *in vacuo* and the residue was fractionated to give 4.2 g (70%) of a colorless oil, bp 76-77° at 8 mm (lit (24) bp 75° at 10 mm).

cis-9,10-Dicarbomethoxy-9,10-dihydroanthracene (II)

9,10-Dihydroanthracene-9,10-*cis*-dicarboxylic anhydride was prepared by the method of Beckett, Lingard and Mulley (57); mp 189-193° (lit (57) mp 194-195°). A solution of 0.7 g of the anhydride in 10 ml of methanol containing 0.1 g concentrated sulfuric acid was refluxed for 4.5 hours. The methanol was removed *in vacuo* and the residue was dissolved in 100 ml benzene. After extracting with 10% sodium hydroxide solution and saturated sodium chloride solution, the organic phase was dried over magnesium sulfate and the benzene was removed *in vacuo*. Recrystallization of the residue from benzene–hexane gave 300 mg white crystals, mp 167-168.5° (lit (58) mp 166-166.5°).

NMR ($CDCl_3$) δ3.55 (s, 6H), δ4.95 (s, 2H) δ7.15-7.55 (multiplet, 8H).

cis-9,10-Dicarbomethoxy-9,10-dideuterioanthracene

9,10-Dibromoanthracene was prepared by the reaction of anthracene with dioxane—dibromide; mp 222-223° (lit (59) mp 225-227°). To 3.5 g (1.17 mole) of a fine dispersion of lithium metal in 200 ml of dry ether was added 27.4 g (0.20 mole) of n-bromobutane during 0.75 hour. This solution was stirred at 0° over a period of 6 hours, then added (under nitrogen) to a suspension of 22.0 g (0.0655 mole) of 9,10-dibromoanthracene in 1500 ml of dry ether at 0° during 30 minutes (60). After stirring an additional 2.5 hours at 0°, 20 ml of deuterium oxide was added and stirring was continued for 1 hour. The phases were separated and the ethereal phase was extracted with saturated sodium chloride solution (2 x 25 ml). The solution was dried over magnesium sulfate, concentrated and the residue was recrystallized from methanol—benzene to give 7.1 g (60%) of white platelets, mp 214-217° (lit (61) mp 219-220°). Mass spectral analysis gave 0.176 atom fraction deuterium in the molecule. The 9,10-dideuteroanthracene was converted to cis-9,10-dicarbomethoxy-9,10-dideuterioanthracene in the same manner as described for the preparation of cis-9,10-dicarbomethoxy-9,10-dihydroanthracene; mp 165-167°. NMR analysis gave 1.56 D at C-9 plus C-10.

NMR ($CDCl_3$) δ3.55 (s, 6H), δ4.95 (s, 0.44H), δ7.15-7.55 (multiplet, 8H).

cis-9,10-Dicarbomethoxy-9-hydro-10-methylanthracene

9-Methylanthracene was prepared by the Wolff-Kishner reduction of 9-anthraldehyde (62); mp 77-79° (lit (63) mp 79-80°). This was converted to cis-9,10-dicarbomethoxy-9-hydro-10-methylanthracene by the method of Beckett and Lingard (64); mp 156-158° (lit (64) mp 160°).

NMR ($CDCl_3$) δ1.94 (s, 3H), δ3.51 (s, 3H), δ3.60 (s, 3H), δ5.11 (s, 1H), δ7.2-7.6 (multiplet, 8H).

Dimethyl homothujadicarboxylate (Vb)

To a solution of 1.0 g of 4-hydroxymethylenethujone (65) in 100 ml 10% sodium hydroxide solution and 65 ml methanol was added 25 ml 30% hydrogen peroxide over a period of 20 minutes. After stirring at ambient temperatures for 17 hours, the solution was cooled to 5° and acidified with cold 50% sulfuric acid. After dilution to 750 ml with water, the solution was saturated with sodium chloride and extracted with ether (3 x 150 ml). The ether extracts were washed with 10% sodium hydroxide solution (3 x 70 ml) and these basic extracts were acidified with 50% sulfuric acid. After saturation with sodium chloride, the solution was extracted with ether. The ethereal solution was dried over magnesium sulfate and concentrated to give 1.0 g of a clear viscous oil, presumably impure homothujadicarboxylic acid (66). This residue was taken up in 50 ml ether and a distilled solution of diazomethane (from 7.0 g Diazald) in 100 ml ether was added.

After standing in the dark for 18 hours, the excess diazomethane was reacted with acetic acid. After dilution of the ethereal solution with 50 ml ether, the solution was washed with saturated sodium bicarbonate solution (3 x 30 ml) followed by saturated sodium chloride solution (30 ml). After drying over magnesium sulfate, the ether was removed in vacuo, leaving 1.2 g crude residue. A pure sample of dimethyl homothujadicarboxylate was obtained by preparative glpc (15% Carbowax 20 M on Chrom W, 170°).

Infrared (CCl_4) 1735, 1725 (non-conjugated and conjugated carbonyls), 1385, 1370, 1165, 1145 (isopropyl), 1295, 1190 (ester), 1035 cm^{-1} (cyclopropane).

NMR (CCl_4) δ0.65-1.28 (multiplet, 13H), δ2.24 (q, J = 7 Hz, 1H), δ3.57 (s, 3H), δ3.60 (s, 3H).

Mass Spec Mol wt 228; found M^+ = 228, prominent peaks at 213 (M-15), 197 (M-31), 181 (M-47), 169 (M-59).

2-Hydroxythymoquinone (X)

Thujone was oxidized by selenium dioxide to 2-hydroxythymoquinone by the method of Eastman and Selover (67); mp 166-169° (lit (67) mp 165-167°).

Mass Spec Mol wt 180; found M^+ = 180.

4-n-Butylthiomethylene-2,2-dimethyl-5-isopropylbicyclo[3.1.0]-hexan-3-one (XI)

To a suspension of 5.4 g (0.10 mole) sodium methoxide

in 45 ml of dry benzene was added 7.2 g (0.047 mole) thujone and 7.4 g (0.10 mole) ethyl formate at 0°. After evacuating, the flask was filled with nitrogen and the solution was stirred at room temperature for 7 hours. After adding 75 ml of ice water, the benzene layer was separated and washed with cold 3N sodium hydroxide solution. The combined aqueous solution was washed with ether, acidified with 5N hydrochloric acid, saturated with sodium chloride and extracted with ether. The ethereal solution was washed with water and saturated sodium chloride solution and dried over magnesium sulfate. After removing the ether, vacuum distillation gave 5.2 g (62%) of a clear liquid (4-hydroxymethylenethujone), bp 89-91° at 3 mm (lit (65) bp 115-118° at 16 mm). To 5.2 g (0.029 mole) of the hydroxymethylene ketone in 50 ml of dry benzene was added 3.0 g (0.033 mole) of n-butylmercaptan and 15 mg p-toluenesulfonic acid. The resulting solution was refluxed for 11 hours with separation of the water produced in a Dean-Starke trap (0.5 ml water). The solution was washed with 10% sodium bicarbonate solution and water. After drying over magnesium sulfate and removal of the benzene in vacuo, vacuum distillation gave 5.0 g (69%) of the thiomethylene ketone, bp 111-119° at 0.25 mm. To a solution of 3.4 potassium metal in 10 ml dry t-butyl alcohol was added 4.5 g of the thiomethylene ketone. After stirring at room temperature for 5 minutes, the mixture was cooled to 0° and 8 ml of methyl

iodide was added. After stirring a few minutes at room temperature and refluxing for 2 hours, most of the solvent was removed and the residual solution was added to 40 ml water. After extracting thoroughly with ether, the combined ethereal extracts were washed with water, the solution was dried over magnesium sulfate, and the ether was removed. There remained 2.4 g of a very viscous orange liquid. The pure compound was obtained by chromatography on alumina followed by recrystallization from methanol, yielding a yellow solid, mp 130-132°.

Infrared (CCl_4) 3060, 1036 (cyclopropyl), 1720 (C=O), 1618 (C=C), 1116, 1082 cm^{-1} (=C–S–C$\lesssim$).

NMR (CCl_4) δ0.22 (broad singlet, 1H), δ0.60-2.30 (multiplet, 22H), δ2.50-3.10 (multiplet, 2H), δ7.27 (s, 1H).

Mass Spec Mol wt 266; found M^+ = 266.

2,2-Dimethyl-6-n-butylthiomethylenecyclohexanone

2,2-Dimethyl-6-n-butylthiomethylenecyclohexanone was prepared by the method of Ireland and Marshall (41) and was purified by chromatography on silica gel followed by vacuum distillation; bp 114-115° at 1 mm (lit (41) bp 89-91° at 0.07 mm).

Sabina ketone (5-isopropylbicyclo[3.1.0]hexan-2-one) (XIIIa)

To a solution of 12.0 g (0.076 mole) potassium permanganate and 3.0 g sodium hydroxide in 80 ml water was added

80 g ice and 4.8 g (0.035 mole) sabinene (Fluka). This was shaken for 1 hour, after which time the manganese dioxide was filtered off and washed with water. The filtrate and washings were concentrated to 20 ml and the residue (3.6 g) was filtered off. The residue was dissolved in 35 ml hot water containing 1.5 ml dilute sulfuric acid. A solution of 2.2 g potassium permanganate and 1.5 g concentrated sulfuric acid in 60 ml water was added dropwise while passing a current of steam through the system. The distillate (50 ml) was salted out with sodium chloride and thoroughly extracted with ether. After drying the ethereal solution over sodium sulfate, the ether was flash distilled, leaving 300 mg of a clear liquid. Pure sabina ketone (68, 69) was isolated by glpc (20% SF-96 on Firebrick, 165°).

Infrared (CCl_4) 3050, 1019 (cyclopropane), 1722 (C=O), 1383, 1364 cm^{-1} ($>C(CH_3)_2$).

NMR (CCl_4) δ0.97-1.20 (multiplet, 8H), δ1.38-1.80 (multiplet, 2H), δ1.85-2.30 (multiplet, 4H).

Derivative Semicarbazone, mp 135-136° (lit (69) mp 135-137°).

5-Methylbicyclo[3.1.0]hexan-2-one

3-Methyl-2-cyclopentenone (70) was reduced with lithium aluminum hydride to the alcohol, bp 77-78° at 30 mm. To a solution of 0.32 mole zinc–copper couple (71) in 250 ml anhydrous ether was added 58 g (0.22 mole) of methylene iodide and 0.1 g iodine crystals. After refluxing gently

for 30 minutes a solution of 8.5 g (0.088 mole) of 3-methyl-2-cyclopentenol in 40 ml ether was added during 45 minutes. After stirring under reflux for 26 hours, 35 ml of saturated ammonium chloride solution was added to precipitate the inorganic salts. The salts were washed with ether and the combined ethereal solution was washed with saturated sodium chloride solution and dried over magnesium sulfate. After removing the ether in vacuo, the residue was added (under nitrogen) to 50 ml of a saturated solution of sodium methoxide in methanol and the mixture was allowed to stand overnight. This mixture was added to 400 ml ether. After extracting with saturated sodium chloride solution until the extracts were neutral, the solution was dried over magnesium sulfate and the ether was removed in vacuo. Fractionation gave 4.3 g (43%) of the bicyclic alcohol, bp 84-85.5° at 28 mm (lit (72) bp 68-70° at 11 mm). The alcohol (4.3 g, 0.038 mole) was oxidized with 12 g (0.12 mole) chromium trioxide in 125 ml pyridine. After stirring at room temperature for twelve hours, the solution was added to 500 ml ether. After extracting with 2% sulfuric acid (6 x 100 ml) and saturated sodium chloride solution (2 x 50 ml), the ethereal solution was dried over magnesium sulfate and concentrated. Fractionation gave 5-methylbicyclo[3.1.0]hexan-2-one, bp 90-94° at 45 mm. An analytical sample was obtained by glpc (20% SF-96 on Firebrick, 150°).

Infrared (CCl_4) 3060, 1020 (cyclopropyl), 1721 cm^{-1} (C=O).

NMR (CCl_4) δ1.04 (t, J = 2.5 Hz, 1H), δ1.10 (s, 1H), δ1.32 (s, 3H), δ1.48 (multiplet, 1H), δ1.98 (t, J = 1.5 Hz, 3H), δ2.10 (doublet of doublets, J = 25 Hz, J = 12.5 Hz, 1H).

Mass Spec Mol wt 110; found M^+ = 110.

Derivative 2,4-Dinitrophenylhydrazone, mp 138-140° (lit (72) mp 138-139°); semicarbazone, mp 148.5-149.5°.

syn-6-(Methoxymethyl)bicyclo[3.1.0]hexan-3-one (XVIa)

syn-Bicyclo[3.1.0]hex-2-en-6-carboxaldehyde (73) was reduced with lithium aluminum hydride to the known bicyclic alcohol (74), bp 77-79° at 9 mm. To a suspension of 6.5 g (0.27 mole) sodium hydride in 300 ml anhydrous ether was added 9.5 g (0.086 mole) of the above alcohol during 45 minutes. After stirring an additional two hours, 45 g of methyl iodide in 50 ml ether was added. After stirring under nitrogen for 69 hours, methanol was added to destroy excess sodium hydride and a saturated ammonium chloride solution was added until the inorganic salts precipitated. After decanting the ethereal solution and washing the salts with ether, the combined ethereal solution was washed with saturated sodium chloride solution. After drying over magnesium sulfate, the ether and excess methyl iodide were distilled off. The residue was fractionated to give 8.8 g

(83%) olefin, bp 76-78° at 47 mm.

To 8.7 g (0.070 mole) of the unsaturated ether in 15 ml dry diglyme was added 0.92 g (0.024 mole) sodium borohydride in 25 ml diglyme (under nitrogen). Then 4.3 g (0.030 mole) boron trifluoride etherate in 10 ml diglyme was added over a period of 1 hour at 5°. After stirring an additional hour at room temperature, 6 ml of water was added, followed by 10 ml of 3N sodium hydroxide. Ten milliliters of 30% hydrogen peroxide was added over a period of 1.5 hours. About 50 ml water was added and the solution was extracted with ether. After drying over magnesium sulfate and distillation of the ether, vacuum distillation gave 3.6 g (36%) of the alcohol, bp 91-94° at 2 mm. A solution of 3.0 g (0.021 mole) of this alcohol in 10 ml pyridine was added to 6 g (0.06 mole) chromium trioxide in 70 ml pyridine. After stirring 11 hours, normal Sarrett workup (75) gave 1.2 g ketone, bp 84-86° at 5 mm. An analytical sample was obtained by glpc (15% Carbowax 20M, 120°).

Infrared (CCl_4) 3050 (cyclopropane), 1740 (C=O), 2800, 1144 cm^{-1} ($-OCH_3$).

NMR (CCl_4) δ1.10-1.95 (multiplet, 3H), δ2.20-2.80 (multiplet, 4H), δ3.18 (d, J = 7 Hz, 2H), δ3.25 (s, 3H).

Mass Spec Mol wt 140; found M^+ = 140.

Derivative 2,4-Dinitrophenylhydrazone, mp 149-150°.

Analysis Calc for $C_{14}H_{16}N_4O_5$: C, 52.52; H, 5.00; N, 17.50.
Found: C, 52.38; H, 5.30; N, 17.29.

Tricyclo[4.3.1.$0^{1,6}$]decan-7-one

4,5,6,7-Tetrahydroindanone was prepared by the method of Mathieson (76); 2,4-dinitrophenylhydrazone, mp 231-232° (lit (77) mp 229-230°). The corresponding allylic alcohol was obtained by reduction with lithium aluminum hydride. A Simmons-Smith reaction on this alcohol (same procedure as described for the preparation of 5-methylbicyclo[3.1.0]hexan-2-ol) gave tricyclo[4.3.1.$0^{1,6}$]decan-7-ol in 49% yield. The ketone, tricyclo[4.3.1.$0^{1,6}$]decan-7-one, was obtained in 92% yield upon Sarrett oxidation (75) with chromium trioxide in pyridine; bp 78-80° at 2 mm. An analytical sample was obtained by preparative glpc (20% DEGS on Chrom W, 153°).

Infrared (CCl_4) 3065, 1022 (cyclopropane), 1715 cm^{-1} (C=O); (lit (78) 3065, 1715 cm^{-1}).

NMR (CCl_4) δ0.85-2.50 (complex multiplet).

Mass Spec Mol wt 150; found M^+ = 150.

Analysis Calc for $C_{10}H_{14}O$: C, 80.00; H, 9.33.
Found: C, 79.96; H, 9.41.

Derivative Semicarbazone, mp 189-190° (D).

9-Methyltricyclo[4.3.1.$0^{1,6}$]decan-7-one

9-Methylbicyclo[4.3.0]non-1-en-7-one was prepared from crotonic acid and cyclohexene by the method of Dev (77); 2,4-dinitrophenylhydrazone, mp 242.5-243° (lit (77) mp 244°).

This was reduced with lithium aluminum hydride to the allylic alcohol, bp 94-95° at 4 mm. A Simmons-Smith reaction with this alcohol (same procedure as for the preparation of 5-methylbicyclo[3.1.0]hexan-2-ol) gave a 68% yield of 9-methyltricyclo[4.3.1.$0^{1,6}$]decan-7-ol, bp 105-106° at 5 mm. Sarrett oxidation (chromium trioxide in pyridine) (75) gave 9-methyltricyclo[4.3.1.$0^{1,6}$]decan-7-one, bp 101-102° at 5 mm.

Infrared (CCl_4) 3065, 1025 (cyclopropane), 1720 cm^{-1} (C=O).

NMR (CCl_4) δ0.9-2.5 (complex multiplet, 13H), δ1.07 (d, J = 6 Hz, 3H).

Mass Spec Mol wt 164; found M^+ = 164

Analysis Calc for $C_{11}H_{16}O$: C, 80.40; H, 9.80.
Found: C, 80.20; H, 9.72.

Derivative 2,4-Dinitrophenylhydrazone, mp 177-177.5°.

Bicyclo[4.1.0]heptan-2-one

Bicyclo[4.1.0]heptan-2-one was prepared by the procedure of Dauben and Berezin (46). An analytical sample was isolated by glpc (15% Carbowax 20M, 168°).

Infrared (CCl_4) 3050, 1026 (cyclopropane), 1695 cm^{-1} (C=O).

NMR (CCl_4) δ0.78-1.26 (multiplet, 2H), δ1.43-2.22 (multiplet, 8H).

Derivative 2,4-Dinitrophenylhydrazone, mp 164-166° (lit (46) mp 159-161.5°).

5,5-Dimethylbicyclo[4.1.0]heptan-2,3-dione (XXVIa)

4,4-Dimethyl-2-cyclohexenone (79) was prepared by the reaction of methyl vinyl ketone with isobutyraldehyde in methanolic potassium hydroxide; 2,4-dinitrophenylhydrazone, mp 139-141° (lit (80) mp 142°). Reduction of the ketone with lithium aluminum hydride gave the allylic alcohol, bp 92-92.5° at 25 mm. The allylic alcohol was subjected to the Simmons-Smith reaction (same conditions as described for the preparation of 5-methylbicyclo[3.1.0]hexan-2-ol) and yielded a 77% yield of the bicyclic alcohol, bp 100-101° at 20 mm. Sarrett oxidation with chromium trioxide in pyridine gave a 77% yield of 5,5-dimethylbicyclo[4.1.0]heptan-2-one, bp 98-100° at 15 mm.

Infrared (CCl_4) 3070, 1025 (cyclopropane), 1168, 1388, 1363 (gem-dimethyl), 1685 cm^{-1} (C=O).

NMR (CCl_4) δ0.80-2.20 (multiplet, 8H), δ1.12 (s, 6H).

Derivative 2,4-Dinitrophenylhydrazone, mp 141-142°.

To a solution of 1.5 g of the above bicyclic ketone in 20 ml 95% ethanol was added 1.3 g selenium dioxide. The mixture was refluxed for 20 hours, diluted with 75 ml methanol and filtered through celite. After the solvent was removed, the residue was taken up in ether and dried over magnesium sulfate. The ether was removed and the crude material was chromatographed on silica gel. Upon elution with 5% ether–hexane, 154 mg of a white crystalline material was obtained.

After two recrystallizations from pentane, the compound melted at 75-77°.

Infrared (KBr) 3400, 1660, 1640 (=C(OH)—C(=O)–), 1020 (cyclopropyl), 1365 cm^{-1} (gem dimethyl).

NMR ($CDCl_3$) δ0.65-0.95 (multiplet, 1H), δ1.30-2.25 (multiplet, 3H), δ1.21 (s, 3H), δ1.29 (s, 3H), δ5.43 (d, J = 2 Hz, 1H), δ5.90 (s, 1H).

Mass Spec Mol wt 152; found M^+ = 152.

Analysis Calc for $C_9H_{12}O_2$: C, 71.00; H, 7.90.

Found: C, 69.60; H, 7.93.

Tricyclo[5.4.0.$0^{1,3}$]undecan-4-one (XXVIIIa)

$\Delta^{1,9}$-Octalone-2 (45) was reduced to the allylic alcohol with lithium aluminum hydride and subjected to the Simmons-Smith reaction (same procedure as described for the preparation of 5-methylbicyclo[3.1.0]hexan-2-ol). The tricyclic alcohol obtained was oxidized in acetone with standard Jones reagent (46). The pure tricyclo[5.4.0.$0^{1,3}$]undecan-4-one was obtained by column chromatography on silica gel followed by preparative glpc (15% Carbowax 20 M, 180°).

Infrared (CCl_4) 3070, 1028 (cyclopropane), 1685 cm^{-1} (C=O).

NMR (CCl_4) δ0.6-2.2 (complex multiplet).

Mass Spec Mol wt 164; found M^+ = 164.

Analysis Calcd for $C_{11}H_{16}O$: C, 80.52; H, 9.75.

Found: C, 80.32; H, 9.75.

Derivative Semicarbazone, mp 213-215 (D).

3-Methyltricyclo[5.4.0.$0^{1,3}$]undecan-4-one (XXIXa)

$\Delta^{1,9}$-1-Methyl-2-octalone (Aldrich Chemical Co.) was reduced to the allylic alcohol with lithium aluminum hydride. A Simmons-Smith reaction on the allylic alcohol (same procedure as described for the preparation of 5-methylbicyclo-[3.1.0]hexan-2-ol) followed by oxidation of the tricyclic alcohol with standard Jones reagent (46) in acetone, gave 3-methyltricyclo[5.4.0.$0^{1,3}$]undecan-4-one. An analytical sample was obtained by column chromatography on silica gel followed by preparative glpc (15% Carbowax 20 M, 180°).

Infrared (CCl_4) 3050, 1020 (cyclopropane), 1680 cm^{-1} (C=O).

NMR (CCl_4) δ0.50 (t, J = 5 Hz, 1H), δ1.0-2.3 (multiplet, 14H), δ1.2 (d, J = 5 Hz, 3H).

Mass Spec Mol wt 178; found M^+ = 178.

Derivative Semicarbazone, mp 203-204°.

Analysis Calcd for $C_{13}H_{21}N_3O$: C, 66.38; H, 8.93.
Found: C, 66.17; H, 9.08.

4,4,6-Trimethylbicyclo[4.1.0]heptan-2-one

Isophorone was reduced to the allylic alcohol with lithium aluminum hydride. A Simmons-Smith reaction with the allylic alcohol (same procedure as described for the preparation of 5-methylbicyclo[3.1.0]hexan-2-ol) gave 4,4,6-trimethylbicyclo[4.1.0]heptan-2-ol. Oxidation with chromium trioxide in pyridine (75) gave 4,4,6-trimethylbicyclo-[4.1.0]heptan-2-one, bp 85-87° at 9 mm. An analytical

sample was obtained by column chromatography on silica gel followed by preparative glpc (15% Carbowax 20 M, 120°).

Infrared (CCl_4) 3040, 1015 (cyclopropane), 1690 cm^{-1} (C=O).

NMR (CCl_4) δ0.94. (s, 6H), δ1.18 (s, 3H), δ0.8-1.9 (multiplet, 7H).

Mass Spec Mol wt 152; found M^+ = 152.

Derivative 2,4-Dinitrophenylhydrazone, mp 128-129.5°.

Methyl cis-3-carbomethoxy-1,1-dimethylcyclopropane-2-propionate

3-Carene was equilibrated with its isomer, 2-carene, by the method of Acharya and Brown (44). cis-3-Carboxy-1,1-dimethylcyclopropane-2-propionic acid (81) was prepared from the mixture of 2- and 3-carene by the method of Piatkowski, Kuzynski and Kubik (82). The crude mixture of diacids was esterfied with diazomethane in ether. The desired diester, methyl cis-3-carbomethoxy-1,1-dimethylcyclopropane-2-propionate, was isolated by preparative glpc (15% Carbowax 20 M, 150°; this diester had a retention time of 6 minutes whereas the other product (dimethyl 1,1-dimethylcyclopropane-cis-2,3-diacetate) had a retention time of 12 minutes under the same conditions).

Infrared (CCl_4) 1735 (nonconjugated C=O), 1720 (conjugated C=O), 1525, 1235, 1162 cm^{-1} (ester).

NMR (CCl_4) δ1.15 (s, 3H), δ1.20 (s, 3H), δ1.10-1.50 (multiplet, 3H), δ1.90 (d, J = 18 Hz, 1H),

δ2.60-2.70 (multiplet, 2H), δ3.57 (s, 3H), δ3.60 (s, 3H).

Mass Spec Mol wt 214; M^+ not observed; prominent peaks at 183 (M-31), 155 (M-59), 127 (M-87).

7-Methyltricyclo[5.4.0.$0^{1,3}$]undecan-4-one (XXXIII)

A solution of dimethyloxosulfonium methylide (0.017 mole) in 25 ml DMSO was prepared by the method of Corey and Chaykovsky (83). To this well stirred solution (under nitrogen) was added a solution of 2.5 g (0.0152 mole) of 10-methyl-1-(9)-octal-2-one (45) in 5 ml DMSO over a period of 35 minutes. After stirring at room temperature for 4.5 hours and at 55° for 1 hour, the mixture was cooled and added to 80 ml cold water. Extraction with ether (3 x 100 ml) followed by drying the ethereal solution over magnesium sulfate and concentration gave 2.6 g crude product. Vacuum distillation gave 1.2 g (44%) of a clear liquid, bp 76-80° at 0.3 mm. An analytical sample was obtained by column chromatography on silica gel followed by preparative glpc (15% Carbowax 20 M, 180°).

Infrared (CCl_4) 3050, 1035 (cyclopropane), 1680 cm^{-1} (C=O).

NMR (CCl_4) δ0.40-0.90 (multiplet, 2H), δ1.10 (s, 3H), δ1.15-2.40 (multiplet, 13H).

Mass Spec Mol wt 178; found M^+ = 178.

Derivative 2,4-Dinitrophenylhydrazone, mp 166-168°.

Methyl cis-2-carbomethoxycyclobutane-1-ethanoate (XXXVIc)

Methanol (2.0 ml) was added to 3.5 g of cis-1,2-cyclobutanedicarboxylic anhydride (Aldrich Chemical Co.) and the mixture was refluxed for 4 hours. The excess methanol was removed in vacuo, leaving crude cis-2-carbomethoxycyclobutanecarboxylic acid. This residue was dissolved in 40 ml dry benzene and a few drops of pyridine and 5 ml of thionyl chloride were added. The flask was equipped with a drying tube and the contents were stirred for 21 hours at room temperature. The benzene was removed in vacuo and the residue was dissolved in 100 ml of dry ether. This was filtered and added dropwise to a solution of diazomethane (from 15 g Diazald) in 200 ml ether. After standing at room temperature for 18 hours, the ether was removed in vacuo. The residue (a bright yellow oil) was added to 60 ml of methanol and a solution of 0.5 g silver benzoate in 5 ml of dry triethyl amine was added in portions over a period of 1 hour. After nitrogen evolution had ceased, the solution was refluxed for 1.5 hour. The mixture was filtered, the methanol was removed in vacuo and the residue was dissolved in 200 ml of ether. After washing with 1N hydrochloric acid, (4 x 25 ml), 10% sodium bicarbonate solution (25 ml) and saturated sodium chloride solution (50 ml), the ethereal solution was dried over magnesium sulfate and concentrated. Vacuum distillation gave 1.6 g of a clear liquid, bp 67-85° at 0.3

mm. This was shown to be a mixture of dimethyl cis-1,2-cyclobutanedicarboxylate and methyl cis-2-carbomethoxycyclobutane-1-ethanoate. An analytical sample of the latter compound was obtained by preparative glpc (15% Carbowax 20 M, 160°).

Infrared (CCl_4) 1740 (C=O), 1435, 1350, 1192, 1165 cm^{-1} (ester).

NMR (CCl_4) δ1.6-2.5 (multiplet, 6H), δ2.8-3.4 (multiplet, 2H), δ3.58 (s, 3H), δ3.60 (s, 3H).

Mass Spec Mol wt 186; found M^+ = 186, prominent peaks at 155 (M-31), 127 (M-59).

Dihydrolumiisocolchicine ketol

To a solution of 30 mg of lumiisocolchicine ketol (XXXVIIa) in 5 ml 95% ethanol was added 5 mg of Adams catalyst and hydrogen was bubbled through the solution for 42 hours. After filtration and removing the ethanol in vacuo, 10 ml of benzene was added. Concentration gave a white crystalline solid, mp 140-145° (lit (47) mp 146-149°).

β-Lumicolchicine ketol

β-Lumicolchicine was reduced to the alcohol with sodium borohydride and hydrolyzed with dilute acid to the ketol (84, 85). Recrystallization from aqueous ethanol gave white crystals, mp 215-218° (lit (85) mp 208°).

1,7-Dimethylbicyclo[3.2.0]hept-6-en-2-one

A solution of 5.0 g of 2-cyclopentenone in 100 ml of 2-butyne was degassed with nitrogen at 0° for 10 minutes and then irradiated, in a quartz vessel with an internal cooling coil, at 3000Å in a Rayonet Photochemical Reactor for 90 hours. The 2-butyne was recovered by distillation and the residue was fractionated. A central fraction, bp 59-63° at 12 mm, was shown to consist of about 80% 1,7-dimethylbicyclo[3.2.0]hept-6-en-2-one and 20% 6,7-dimethylbicyclo-[3.2.0]hept-6-en-2-one (86, 87). Higher boiling fractions contained almost exclusively the latter compound. An analytical sample of 1,7-dimethylbicyclo[3.2.0]hept-6-en-2-one was obtained by preparative glpc (15% Carbowax 20 M, 130°).

Infrared (CCl_4) 1720 (C=O), 3030, 1630 cm^{-1} (C=C).

NMR (CCl_4) δ1.14 (s, 3H), δ1.57 (t, J = 1.5 Hz, 3H), δ1.7-3.0 (multiplet, 5H) δ5.85 (t, J = 1.5 Hz, 1H).

Mass Spec Mol wt 136; found M^+ = 136.

Derivative 2,4-Dinitrophenylhydrazone, mp 170-172° (lit (86) mp 171-172°).

1,4,4-Trimethylbicyclo[3.2.0]heptan-2,3-dione

To a solution of 2.5 g (0.016 mole) of 1,4,4-trimethylbicyclo[3.2.0]heptan-2-one in 20 ml of 95% ethanol was added 2.0 g (0.018 mole) of selenium dioxide and the mixture was refluxed for twelve hours. After cooling 100 ml of methanol was added and the suspension was filtered through a Celite

column to remove elemental selenium. After adding 10 ml benzene, the combined solvent was removed by distillation. The residue was chromatographed on silica gel, the diketone being eluted with 2% ether in hexane. After sublimation (50° at 10 mm) and two recrystallizations from pentane, 1.20 g (45%) of bright orange crystals were obtained, mp 57-58°.

Infrared (CCl_4) 1765, 1750 (), 1387, 1375, 1220, 1200 cm^{-1} ($>C(CH_3)_2$).

NMR (CCl_4) δ1.01 (s, 3H), δ1.17 (s, 3H), δ1.39 (s, 3H) δ1.5-2.8 (multiplet, 5H).

Mass Spec Mol wt 166; found M^+ = 166, prominent peaks at 138 (M-28), 123 (M-43), 109 (M-57).

1,4,4-Trimethylbicyclo[3.2.0]hept-6-en-2,3-dione

A solution of 2.5 g (0.017 mole) of 1,4,4-trimethylbicyclo[3.2.0]hept-6-en-2-one and 2.0 g (0.018 mole) of selenium dioxide in 20 ml of 95% ethanol was refluxed for 26 hours. After workup (as described for the saturated dione) and chromatography on silica gel, elution with 5% ether in hexane gave 150 mg (5%) of a yellow crystalline compound. After two low temperature recrystallizations from pentane, the dione melted at 75-76°.

Infrared (CCl_4) 1770, 1750 (), 1660 (C=C), 1385, 1375 cm^{-1} ($>C(CH_3)_3$).

NMR ($CDCl_3$) δ1.02 (s, 3H), δ1.20 (s, 3H), δ1.53 (s, 3H), δ2.90 (s, 1H), δ5.86 (d, J = 2.5 Hz, 1H), δ6.50

(d, J = 2.5 Hz, 1H).

Mass Spec Mol wt 164; found M^+ = 164, prominent peaks at 136 (M-28), 121 (M-43), 108 (M-56), 107 (M-57).

Tricyclo[3.3.2.$0^{1,5}$]dec-9-en-2-one

A solution of 7.0 g of bicyclo[3.3.0]oct-1(5)-en-2-one and 100 ml of 1,2-dichloroethylene (about 75% cis) in 500 ml of pentane was degassed with nitrogen for 1 hour and then irradiated in Pyrex with a Hanovia 550 watt lamp until the 1695 cm^{-1} band in the infrared (due to the enone) was completely replaced by a band at 1740 cm^{-1} (due to the saturated ketone) (about 12 hours). The solvent was removed in vacuo leaving 15.0 g of a light brown viscous residue. This crude product was combined with 4.5 ml of ethylene glycol and 50 mg of p-toluenesulfonic acid in 100 ml of benzene. This solution was refluxed for 12 hours with separation of the water produced in a Dean-Starke trap. After extracting with saturated sodium chloride solution (2 x 25 ml) and drying over magnesium sulfate, concentration gave 15.0 g of a mixture of the isomeric ketals. This crude product, in 125 ml ether, was added to 350 ml of liquid ammonia and 5.0 g of sodium metal was added over a period of 15 minutes. After stirring an additional two hours, an excess (15 g) of ammonium chloride was added and the ammonia was slowly evaporated. To the residue was added 150 ml of water and the solution was extracted well with ether

(3 x 150 ml). The ethereal solution was washed with water (2 x 20 ml) and saturated sodium chloride solution (2 x 20 ml), and dried over magnesium sulfate. The ether was removed *in vacuo*, leaving 9.6 g of an orange oil. This was added to 40 ml of ether and 20 ml of 3N hydrochloric acid was added. After stirring at room temperature for five hours, the phases were separated and the aqueous phase was extracted with ether (3 x 75 ml). The combined ethereal extracts were washed with water (2 x 25 ml) and saturated sodium chloride solution (2 x 15 ml). After drying over magnesium sulfate the ether was removed *in vacuo* and the crude residue (7.8 g) was fractionated, giving 5.0 g of the tricyclic ketone, bp 83-84° at 10 mm. An analytical sample was obtained by preparative glpc (15% Carbowax 20 M, 150°).

Infrared (CCl_4) 1725 (C=O), 1675 cm^{-1} (C=C).

NMR (CCl_4) δ0.8-3.5 (complex multiplet).

Derivative Semicarbazone, mp 187-190 (D) (lit (88) mp 185°).

Tricyclo[3.3.2.$0^{1,5}$]decan-2-one

To a solution of 1.0 g of tricyclo[3.3.2.0]dec-9-en-2-one (described previously) in 30 ml of benzene was added 200 mg of 10% palladium on charcoal and hydrogen was bubbled through the stirred solution for 36 hours. After filtration, the benzene was removed *in vacuo*. An analytical sample was obtained by preparative glpc (15% Carbowax 20 M, 170°); mp 61-63°.

Infrared (CCl_4) 1730 cm^{-1} (C=O).

NMR (CCl_4) δ1.3-3.2 (complex multiplet).

Mass Spec Mol wt 150; found M^+ = 150.

Derivative Semicarbazone, mp 203-206° (D), (lit (88) mp 200-202° (D)).

9,10-Dimethyltricyclo[3.3.2.$0^{1,5}$]dec-9-en-2-one

A solution of 7.6 g bicyclo[3.3.0]oct-1(5)-en-2-one in 120 ml of dry benzene was degassed for 45 minutes with nitrogen and 10.0 g of 2-butyne was added. The solution was irradiated at 2537Å in a Rayonet reactor at 15° for 14 days. The solvent was removed in vacuo and the residue was vacuum distilled to give 7.4 g of product, bp 94-95° at 8 mm. An analytical sample was obtained by preparative glpc (20% DEGS, 170°).

Infrared (CCl_4) 1725 (C=O), 1680 cm^{-1} (C=C).

NMR (CCl_4) δ1.0-3.3 (complex multiplet).

Derivative Semicarbazone, mp 217° (D) (lit (89) mp 214° (D)).

Dimethyl cis-1,3-cyclobutanedicarboxylate (LVIb)

Dimethyl cis-1,3-cyclobutanedicarboxylate was prepared by the method of Allinger and Tushaus (90). An analytical sample was obtained by preparative glpc (20% SF-96, 150°).

Dimethyl bicyclo[2.1.1]hexane-syn, exo-5,6-dicarboxylate

Tricyclo[3.3.0.$0^{2,6}$]oct-3-ene was prepared by the method of Meinwald and Kaplan (91). Ozone was bubbled through a solution of 200 mg of the olefin in 25 ml of methanol at -75°

until the solution retained the purple color. The methanol was removed *in vacuo* and the residue was dissolved in 10 ml formic acid and 5 ml 30% hydrogen peroxide. After stirring at room temperature for 12 hours and refluxing for 1 hour, the solvent was removed *in vacuo* leaving about 250 mg of a crystalline residue. This crude material was dissolved in 30 ml ether and reacted with diazomethane (from 4.0 g Diazald) in 50 ml ether. After standing at room temperature for 16 hours, the excess diazomethane was decomposed with acetic acid and the ethereal solution was washed with saturated sodium bicarbonate solution (2 x 25 ml) and saturated sodium chloride solution (25 ml) and dried over magnesium sulfate. Concentration of the solution, low temperature recrystallization from pentane and preparative glpc (15% Carbowax 20 M, 160°) gave 125 mg of white crystalline material, mp 84-86°.

Infrared (CCl_4) 1735 (C=O), 1340, 1200, 1162 cm^{-1} (ester).

NMR (CCl_4) δ1.82 (s, 4H), δ2.24 (s, 2H), δ3.04 (s, 2H), δ3.60 (s, 6H).

Mass Spec Mol wt 198; found M^+ = 198, prominent peaks at 167 (M-31), 139 (M-59).

Analysis Calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.11.
Found: C, 60.51; H, 7.09.

Dimethyl 2,2-dimethyl-*cis*-1,3-cyclobutanedicarboxylate

cis-Norpinic acid was prepared by the method of Perkin and Simonsen (92). The crude diacid was refluxed with methanol

and a trace of sulfuric acid to yield dimethyl 2,2-dimethyl-cis-1,3-cyclobutanedicarboxylate. An analytical sample was obtained by preparative glpc (15% Carbowax 20 M, 160°).

Infrared (CCl_4) 1740 (C=O), 1385, 1370 ($\rangle C(CH_3)_3$), 1335, 1190, 1165 cm^{-1} (ester).

NMR (CCl_4) δ0.90 (s, 3H), δ1.30 (s, 3H), δ1.85-2.70 (multiplet, 2H), δ2.64 (t, J = 4 Hz, 2H), δ3.61 (s, 6H).

Mass Spec Mol wt 200; found M^+ = 200, prominent peaks at 169 (M-31), 141 (M-59), 140 (M-60).

Dimethyl cis-1,3-dimethyl-cis-1,3-cyclobutanedicarboxylate

Dimethyl cis-1,3-dimethyl-cis-1,3-dicarboxylate was prepared by the method of LaLonde and Aksentijevich (93). An analytical sample was obtained by preparative glpc (15% Carbowax 20 M, 160°). Infrared and NMR data were in agreement with the reported values.

Dimethyl cis-2,2,4,4-tetramethyl-1,3-cyclobutanedicarboxylate (LXa)

cis-2,2,4,4-Tetramethyl-1,3-cyclobutanedicarboxylic acid was prepared according to the procedure of Lautenschlaeger and Wright (94); mp 230-232° (lit (94) mp 235-236°). Esterification with diazomethane in ether gave the dimethyl ester which was purified by preparative glpc (15% Carbowax 20 M, 155°).

NMR (CCl_4) δ1.27 (s, 12H), δ2.63 (s, 2H), δ3.60 (s, 6H).

Mass Spec Mol wt 228; M^+ not observed; prominent peaks at 213 (M-15), 197 (M-31), 181 (M-47).

Dimethyl methylsuccinate

To a solution of 5.0 g citraconic anhydride (Aldrich Chemical Co.) in 30 ml of methanol was added 0.2 g sulfuric acid and the solution was refluxed for 36 hours. After removing the methanol *in vacuo*, dissolving the residue in ether, extracting with saturated sodium bicarbonate solution and drying over magnesium sulfate, concentration gave 6.0 g of dimethyl citroconate. To a solution of 2.0 g of this diester in 75 ml of benzene was added 0.6 g of 10% palladium on charcoal and hydrogen was bubbled through the stirred solution for 72 hours. After filtration, the solvent was removed *in vacuo* leaving 2.0 g crude product. An analytical sample of dimethyl methylsuccinate (95) was obtained by preparative glpc (15% Carbowax 20 M, 155°).

Infrared (CCl_4) 1742 (C=O), 1440, 1195, 1163 cm^{-1} (ester).

NMR (CCl_4) δ1.18 (d, J = 7 Hz, 3H), δ2.20-3.10 (multiplet, 3H), δ3.63 (s, 6H).

Dimethyl *cis*-bicyclo[2.2.2]octane-2,3-dicarboxylate

cis-Bicyclo[2.2.2]octane-2,3-dicarboxylic acid (96) was esterified with diazomethane in ether. An analytical sample of dimethyl *cis*-bicyclo[2.2.2]octane-2,3-dicarboxylate was obtained by preparative glpc (20% DEGS, 200°).

Infrared (CCl_4) 1740 (C=O), 1430, 1190, 1162 cm^{-1} (ester).

NMR (CCl_4) δ1.2-2.1 (multiplet, 10H), δ2.80 (s, 2H), δ3.56 (s, 6H).

Dimethyl cis, endo-bicyclo[2.2.2]oct-5-ene-2,3-dicarboxylate

To 1.0 g of endo-bicyclo[2.2.2]octa-5-ene-2,3-dicarboxylic anhydride (Aldrich Chemical Co.) was added 0.5 ml methanol and the mixture was refluxed for 4 hours. After removal of the excess methanol, the residue was reacted with diazomethane (from 2.0 g Diazald) in 50 ml of ether. The solution was washed with 10% sodium hydroxide solution (2 x 15 ml) and saturated sodium chloride solution (2 x 15 ml). The ethereal solution was dried over magnesium sulfate and concentrated. Recrystallization from ether-hexane gave 600 mg of white crystals, mp 69-71° (lit (97) mp 69-71°).

Infrared (CCl_4) 1750 (C=O), 1435, 1192, 1162 cm^{-1} (ester).

NMR (CCl_4) δ1.1-1.8 (multiplet, 4H), δ2.9 (broad singlet, 2H), δ3.00 (s, 2H), δ3.56 (s, 6H), δ6.30 (doublet of doublets, J = 5 Hz, J = 3 Hz, 2H).

Dimethyl anti-tricyclo[4.2.2.$0^{2,5}$]deca-3,7-diene-endo, endo-7,8-dicarboxylate

Tricyclo[4.2.2.$0^{2,5}$]deca-3,7-diene-endo-9,10-dicarboxylic anhydride was prepared by the method of Reppe, Schlichting, Klager and Toepel (98). Reaction of this anhydride with methanol and a trace of sulfuric acid under reflux for 8 hours gave the diester, mp 51-52.5° (lit (98) mp 52-55°).

NMR (CCl_4) δ2.70 (broad singlet, 2H), δ2.78 (s, 4H), δ3.52 (s, 6H), δ5.78 (s, 2H), δ5.90 (doublet of doublets, J = 4.5 Hz, J = 3 Hz, 2H).

Dimethyl anti-tricyclo[4.2.2.$0^{2,5}$]decane-endo, endo-7,8-dicarboxylate

To a solution of 1.0 g of the above diester in 25 ml of benzene was added 0.3 g of 10% palladium on charcoal and hydrogen was bubbled through the stirred solution for 14 days. After filtration, the benzene was removed in vacuo. Recrystallization from hexane gave 0.7 g of colorless needles, mp 62-63° (lit (98) mp 60-62°).

NMR (CCl_4) δ1.81 (s, 4H), δ1.90 (broad singlet, 2H), δ2.12 (d, J = 4 Hz, 4H), δ2.38 (multiplet, 2H), δ2.62 (s, 2H), δ3.58 (s, 6H).

Dimethyl pentacyclo[4.4.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]decane-endo, endo-9,10-dicarboxylate

This diester was prepared by the method of Dauben and Whalen (99). The pure compound was obtained by chromatography on silica gel, mp 81-82 (lit (99) mp 81-82°). The NMR spectrum was in agreement with the published data.

Dimethyl 9,10-dihydro-9,10-ethanoanthracene-cis-11,12-dicarboxylate

9,10-Dihydro-9,10-ethanoanthracene-11,12-dicarboxylic anhydride was prepared by the method of Bachmann and Scott (100). A solution of 3.7 g of this anhydride in 20 ml of

methanol containing 0.2 ml sulfuric acid was refluxed for 21 hours. The methanol was removed *in vacuo* and the residue was dissolved in 100 ml benzene. Extraction with 10% sodium hydroxide (2 x 15 ml) and saturated sodium chloride solution (15 ml), drying over magnesium sulfate, concentration and recrystallization of the residue from hexane gave 3.6 g white needles, mp 152-153° (lit (101) mp 150-150.5°).

Infrared (KBr) 1740 cm^{-1} (C=O).

NMR ($CDCl_3$) δ3.20 (d, J = 1 Hz, 2H), δ3.49 (s, 6H), δ4.59 (d, J = 1 Hz, 2H), δ7.00-7.40 (multiplet, 8H).

Mass Spec Mol wt 322; found M^+ = 322, prominent peaks at 291 (M-31), 263 (M-59), 178 (M-144).

Dimethyl 9,10-dideuterio-9,10-ethanoanthracene-cis-11,12-dicarboxylate

Dimethyl 9,10-dideuterio-9,10-ethanoanthracene-*cis*-11,12-dicarboxylate was prepared from 9,10-dideuterioanthracene (preparation described previously) by the same procedure as described for the 9,10-dihydro- compound. Upon recrystallization from benzene-hexane, colorless needles were obtained, mp 151-152°.

Infrared (KBr) 2180 (C-D), 1740 cm^{-1} (C=O).

NMR ($CDCl_3$) δ3.19 (s, 2H), δ3.48 (s, 6H), δ7.00-7.40 (multiplet, 8H).

Mass Spec Mol wt 324; found M^+ = 324, prominent peaks at 293 (M-31), 265 (M-59), 180 (M-144).

Dimethyl 9-methyl-10-hydro-9,10-ethanoanthracene-cis-11,12-dicarboxylate

9-Methyl-9-hydro-9,10-ethanoanthracene-11,12-dicarboxylic anhydride was prepared by the method of Bachmann and Kloetzel (101); mp 268-270° (lit (101) mp 264-266°). A solution of 0.8 g of this anhydride in 40 ml of methanol containing 0.2 ml sulfuric acid was refluxed for 42 hours. The methanol was removed and the residue was dissolved in 100 ml benzene. After washing with 10% sodium hydroxide (2 x 20 ml) and saturated sodium chloride solution (20 ml), the solution was dried over magnesium sulfate and the benzene was removed *in vacuo*. Recrystallization from benzene-hexane gave 0.6 g of white crystals, mp 165-167°.

Infrared (KBr) 1730 cm^{-1} (C=O).

NMR ($CDCl_3$) δ1.93 (s, 3H), δ3.11 (d, J = 1 Hz, 2H), δ3.44 (s, 3H), δ3.48 (s, 3H), δ4.60-4.70 (multiplet, 1H), δ7.00-7.55 (multiplet, 8H).

Mass Spec Mol wt 336; found M^+ = 336, prominent peaks at 305 (M-31), 277 (M-59), 192 (M-144).

Dimethyl 9,10-dimethyl-9,10-ethanoanthracene-cis-11,12-dicarboxylate

9,10-Dimethyl-9,10-ethanoanthracene-11,12-dicarboxylic anhydride was prepared by the method of Andrews and Keefer (102) from 9,10-dimethylanthracene (103). A solution of 1.0 g of the anhydride in 30 ml of methanol containing 0.2 ml

sulfuric acid was refluxed for 21 days (reaction still incomplete). After filtering off the unchanged anhydride, the methanol was removed in vacuo and the residue was dissolved in 50 ml benzene. After washing with 10% sodium hydroxide (2 x 10 ml) and saturated sodium chloride solution (10 ml), the solution was dried over magnesium sulfate and concentrated. Recrystallization from benzene-hexane gave 100 mg of colorless cubes, mp 211-214° (lit (104) mp 209-211°).

Infrared (KBr) 1740 cm^{-1} (C=O).

NMR ($CDCl_3$) δ2.00 (s, 6H), δ3.06 (s, 2H), δ3.45 (s, 6H), δ7.00-7.45 (multiplet, 8H).

Mass Spec Mol wt 350; found M^+ = 350, prominent peaks at 319 (M-31), 291 (M-59), 206 (M-144).

Dimethyl 2,3-dimethylbicyclo[2.2.2]oct-5-ene-endo, endo-2,3-dicarboxylate

Dimethyl 2,3-dimethylbicyclo[2.2.2]oct-5-ene-endo, endo-2,3-dicarboxylate was prepared by the method of Ziegler, Flaig and Velling (105).

Dimethyl bicyclo[4.2.0]octane-exo, exo-2,5-dicarboxylate

To a solution of 6.7 g (0.03 mole) of tricyclo[4.2.2.$0^{2,5}$]-decane-endo, endo-9,10-dicarboxylic acid (98) in 75 ml of dry benzene was added 4.8 g (0.060 mole) of pyridine. The solution was cooled to 0° and 17.0 g (0.035 mole) of lead tetraacetate was added. After stirring at room temperature (under nitrogen) for 72 hours, 150 ml of benzene and 100 ml of water was added.

The phases were separated and the benzene solution was extracted with 10% sodium hydroxide (4 x 50 ml) and saturated sodium chloride solution (40 ml). After drying over magnesium sulfate the benzene was removed *in vacuo*, leaving 2.0 g of crude *anti*-tricyclo[4.2.2.$0^{2,5}$]oct-7-ene. A solution of 900 mg of this olefin was ozonized in 25 ml ethyl acetate at -78°. The ethyl acetate was removed at reduced pressure and the residue was added to a mixture of 15 ml of 90% formic acid and 5 ml of 30% hydrogen peroxide. After stirring at room temperature for 24 hours, the solvent was removed at reduced pressure. The residue was added to 40 ml of methanol containing 0.2 ml sulfuric acid and the solution was refluxed for 17 hours. The methanol was removed *in vacuo* and the residue was dissolved in 100 ml of ether. The ethereal solution was washed with saturated sodium bicarbonate solution (25 ml) and saturated sodium chloride solution (30 ml). After drying over magnesium sulfate, the ether was removed at reduced pressure. An analytical sample was obtained by preparative glpc (15% Carbowax 20 M, 180°).

Infrared (CCl_4) 1725 cm^{-1} (C=O).

NMR (CCl_4) δ1.6-2.8 (multiplet, 12H), δ3.59 (s, 6H).

Mass Spec Mol wt 226; found M^+ = 226, prominent peaks at 195 (M-31), 167 (M-59).

Dimethyl octahydro-exo-4,7-methanoindene-exo, exo-1,3-dicarboxylate

Octahydro-exo-4,7-methanoindene-exo, exo-1,3-dicarboxylic acid was prepared by the method of Soloway (106); mp 259-261° (lit (106) mp 256°). This was converted to the dimethyl ester by refluxing with methanol containing a trace of sulfuric acid. Recrystallization from hexane gave white platelets, mp 97-99°.

Infrared (KBr) 1735 (C=O), 1435, 1240, 1192, 1150 cm^{-1} (ester).

NMR (CCl_4) δ0.8-3.0 (multiplet, 14H), δ3.65 (s, 6H).

Mass Spec Mol wt 252; found M^+ = 252, prominent peaks at 221 (M-31), 193 (M-59).

Dimethyl 5-norbornene-endo, endo-2,3-dicarboxylate

This diester was prepared by the method of Bode (107).

NMR (CCl_4) δ1.30-1.42 (multiplet, 2H), δ3.02-3.15 (multiplet, 2H), δ3.18 (t, J = 1.5 Hz, 2H), δ3.50 (s, 6H), δ6.12 (t, J = 1.5 Hz, 2H).

Dimethyl endo, endo-2,3-norbornanedicarboxylate

To a solution of 500 mg of dimethyl 5-norbornene-endo, endo-2,3-dicarboxylate in 15 ml of dry benzene was added 100 mg of 10% palladium on charcoal and hydrogen was bubbled through the stirred solution for 18 hours. After filtration, the benzene was removed in vacuo. An analytical sample of dimethyl endo, endo-2,3-norbornanedicarboxylate (107) was

obtained by preparative glpc (20% DEGS, 195°).

NMR (CCl_4) δ1.20-1.90 (multiplet, 6H), δ2.35-2.55 (multiplet, 2H) δ2.80-2.90 (multiplet, 2H), δ3.55 (s, 6H).

Dimethyl 5-norbornene-*exo*, *exo*-2,3-dicarboxylate

This diester was prepared by the method of Bode (107).

NMR (CCl_4) δ1.40 (doublet of multiplets, J = 9 Hz, 1H), δ2.10 (doublet of multiplets, J = 9 Hz, 1H), δ2.51 (d, J = 2 Hz, 2H), δ3.02 (p, J = 2 Hz, 2H), δ3.57 (s, 6H), δ6.17 (t, J = 2 Hz, 2H).

Dimethyl *exo*, *exo*-2,3-norbornanedicarboxylate

Dimethyl 5-norbornene-*exo*, *exo*-2,3-dicarboxylate was hydrogenated in benzene in the presence of 10% palladium on charcoal to give the saturated diester (107). An analytical sample was obtained by preparative glpc (20% DEGS, 195°).

NMR (CCl_4) δ1.05-1.70 (multiplet, 5H), δ2.01 (doublet of multiplets, J = 10 Hz, 1H), δ2.40-2.55 (multiplet, 2H), δ2.58 (d, J = 1.5 Hz, 2H), δ3.51 (s, 6H).

Dimethyl *exo*, *exo*-5,6-dideuterionorbornane-*exo*, *exo*-2,3-dicarboxylate

To a solution of 250 mg of dimethyl 5-norbornene-*exo*, *exo*-2,3-dicarboxylate in 15 ml of benzene was added 50 mg of 10% palladium on charcoal and deuterium gas was bubbled through the stirred solution for 24 hours. After filtration and

removal of the benzene *in vacuo*, an analytical sample of the saturated diester was obtained by preparative glpc (20% DEGS, 180°).

Infrared (CCl_4) 2175 (C-D), 1740 cm^{-1} (C=O).

NMR (CCl_4) δ1.05-1.32 (multiplet, 3H), δ2.04 (doublet of multiplets, J = 10 Hz, 1H), δ2.49 (t, J = 1.5 Hz, 2H), δ2.60 (d, J = 1.5 Hz, 2H), δ3.52 (s, 6H).

Dimethyl tetracyclo[3.2.1.$1^{3,8}$.$0^{2,4}$]nonane-*endo*, *endo*-6,7-dicarboxylate

Dimethyl tetracyclo[3.2.1.$1^{3,8}$.$0^{2,4}$]non-6-ene-6,7-dicarboxylate was obtained by refluxing equimolar amounts of norbornadiene and dimethyl acetylenedicarboxylate (108); mp 66-67° (lit (109) mp 64°). Hydrogenation in benzene in the presence of 10% palladium on charcoal gave dimethyl tetracyclo[3.2.1.$1^{3,8}$.$0^{2,4}$]nonane-*endo*, *endo*-6,7-dicarboxylate, mp 64-66° (lit (109) mp 61-62°).

Infrared (CCl_4) 3060 (cyclopropane), 1730 cm^{-1} (C=O).

NMR (CCl_4) δ1.10-1.35 (multiplet, 3H), δ1.48 (t, J = 1 Hz, 2H), δ1.79 (broad singlet, 1H), δ2.21 (broad singlet, 2H), δ3.08 (t, J = 1.5 Hz, 2H), δ3.57 (s, 6H).

Dimethyl 7-isopropylidine-*exo*, *exo*-2,3-norbornanedicarboxylate

7-Isopropylidine-5-norbornene-*exo*-2,3-dicarboxylic anhydride was prepared by the procedure of Alder and Rühmann

(110), mp 134-135° (lit (110) mp 137°). This was converted to dimethyl 7-isopropylidine-5-norbornene-exo, exo-2,3-dicarboxylate by refluxing with methanol and a trace of sulfuric acid; mp 74-76°. To a solution of 1.5 g of the unsaturated dimethyl ester in 50 ml of absolute ethanol was added 0.4 g of 10% palladium on charcoal and the mixture was shaken on a Parr Hydrogenator under 30 psi hydrogen pressure for 48 hours. After filtration and removal of the solvent in vacuo, recrystallization from hexane gave 1.4 g of white crystals, mp 104-106° (lit (110) mp 114°).

Infrared (CCl_4) 1720 cm^{-1} (C=O).

NMR (CCl_4) δ1.20-1.70 (multiplet, 4H), δ1.67 (s, 6H), δ2.67 (s, 2H), δ2.90 (t, J = 2 Hz, 2H), δ3.50 (s, 6H).

Mass Spec Mol wt 252; found M^+ = 252, prominent peaks at 221 (M-31), 193 (M-59), 192 (M-60).

Dimethyl bicyclo[3.2.2]non-8-ene-endo, endo-6,7-dicarboxylate

Bicyclo[3.2.2]non-8-ene-endo, endo-6,7-dicarboxylic anhydride was prepared by refluxing a solution of equimolar quantities of 1,3-cycloheptadiene and maleic anhydride in xylene for 5 hours. After removing the xylene and recrystallization of the residue from hexane, the adduct was obtained as white crystals, mp 104-105° (lit (111) mp 110-111°). The anhydride was refluxed with methanol and a trace of sulfuric acid for 5 hours. The methanol was removed, the

residue was dissolved in ether and the ethereal solution was extracted with 10% sodium hydroxide solution. After drying the ethereal solution the ether was removed in vacuo. Recrystallization from hexane gave the pure dimethyl ester, mp 57-58°.

Infrared (KBr) 3010, 1645 (C=C), 1740 (C=O), 1440, 1360, 1210, 1192, 1160 cm^{-1} (methyl ester).

NMR (CCl_4) δ1.45-1.65 (multiplet, 6H), δ2.70-3.00 (multiplet, 2H), δ3.10 (s, 2H), δ3.50 (s, 6H), δ5.99 (doublet of doublets, J = 5 Hz, J = 3 Hz, 2H).

Dimethyl cis-1,2-cyclopropanedicarboxylate

cis-Cyclopropanedicarboxylic anhydride was prepared by the method of McCoy (112); mp 56-58° (lit (112) mp 58-60°). The anhydride (1.4 g) was refluxed for 30 minutes with 1.5 ml of water. After evaporation of the water, recrystallization of the residue from nitromethane gave 0.5 g of white crystals, mp 140-142° (lit (112) mp 139-142°). Esterification with diazomethane in ether gave dimethyl cis-1,2-cyclopropanedicarboxylate. An analytical sample was obtained by preparative glpc (20% DEGS, 165°).

Infrared (CCl_4) 3070, 1045 (cyclopropane), 1730 cm^{-1} (C=O).

NMR (CCl_4) δ0.96-2.12 (multiplet, 4H), δ3.61 (s, 6H).

Dimethyl cis-1,2-cyclobutanedicarboxylate (CIII)

cis-1,2-Cyclobutanedicarboxylic anhydride (Aldrich Chemical Co.) was refluxed with methanol and a trace of sulfuric

acid for 4 hours. After removing the methanol *in vacuo*, dissolving the residue in ether, extracting with saturated sodium carbonate solution and drying the ethereal solution over magnesium sulfate, the ether was removed at reduced pressure. An analytical sample of dimethyl *cis*-1,2-cyclobutanedicarboxylate (113) was obtained by preparative glpc (15% Carbowax 20 M, 150°).

NMR (CCl_4) δ2.10 (d, J = 9 Hz, 4H), δ3.28 (t, J = 9 Hz, 2H), δ3.61 (s, 6H).

Dimethyl *cis*-1,2-cyclohexanedicarboxylate

Hexahydrophthalic anhydride (Aldrich Chemical Co.) was converted to dimethyl *cis*-1,2-cyclohexanedicarboxylate (114) by the same method as described for the preparation of CIII. Vacuum distillation gave the pure diester, bp 93-94° at 2 mm (lit (114) bp 136° at 18 mm).

NMR (CCl_4) δ1.12-2.13 (multiplet, 8H), δ2.55-2.88 (multiplet, 2H), δ3.60 (s, 6H).

7,8-Bis(trimethylsiloxy)bicyclo[4.2.0]oct-7-ene

To a refluxing dispersion of 0.3 g sodium sand in 25 ml of toluene (under nitrogen) was added 4 ml of chlorotrimethylsilane and 0.25 g of dimethyl *cis*-1,2-cyclohexanedicarboxylate was added over a period of 15 minutes. After refluxing for 5 hours, the solution was cooled, filtered, and the toluene was removed at reduced pressure. An analytical sample of 7,8-bis(trimethylsiloxy)bicyclo[4.2.0]oct-7-

ene (26) was obtained by preparative glpc (15% Carbowax 20 M, 165°).

NMR (CCl_4) δ0.18 (s, 18H), δ1.50 (broad absorption, 8H), δ2.45 (broad absorption, 2H).

Dimethyl cis-cyclohex-4-ene-1,2-dicarboxylate

This diester was prepared from cis-cyclohex-4-ene-1,2-dicarboxylic anhydride (Aldrich Chemical Co.) by the method described for the preparation of CIII. Vacuum distillation gave the pure diester, bp 93-94° at 1.5 mm (lit (115) bp 130-131° at 14 mm).

NMR (CCl_4) δ2.25-2.54 (multiplet, 4H), δ2.75-3.05 (multiplet, 2H), δ3.60 (s, 6H), δ5.58 (t, J = 1.5 Hz, 2H).

7,8-Bis(trimethylsiloxy)bicyclo[4.2.0]octa-3,7-diene

To a suspension of 0.8 g sodium sand in 75 ml of refluxing toluene (under nitrogen) was added 2 ml of chlorotrimethylsilane followed by 1.0 g of dimethyl cis-cyclohex-4-ene-1,2-dicarboxylate over a period of 45 minutes. After refluxing an additional 4.5 hours (4 ml additional chlorotrimethylsilane being added in 1 ml portions at regular intervals throughout this period), the solution was cooled, filtered and the toluene was removed at reduced pressure. An analytical sample of 7,8-bis(trimethylsiloxy)bicyclo[4.2.0]-octa-3,7-diene (26) was obtained by preparative glpc (15% Carbowax 20 M, 170°).

NMR (CCl_4) δ0.15 (s, 18H), δ1.87-2.16 (multiplet, 4H), δ2.46-2.68 (multiplet, 2H), δ5.48-5.65 (multiplet, 2H).

Dimethyl 4,5-dimethylcyclohex-4-ene-cis-1,2-dicarboxylate

4,5-Dimethylcyclohex-4-ene-cis-1,2-dicarboxylic anhydride (116) was converted to dimethyl 4,5-dimethylcyclohex-4-ene-cis-1,2-dicarboxylate by the same procedure as employed in the preparation of CIII. An analytical sample was obtained by preparative glpc (15% Carbowax 20 M, 165°).

NMR (CCl_4) δ1.60 (s, 6H), δ2.15-2.45 (multiplet, 4H), δ2.73-3.03 (multiplet, 2H), δ3.60 (s, 6H).

4,5-Dimethyl-7,8-bis(trimethylsiloxy)bicyclo[4.2.0]octa-3,7-diene

To 0.4 g of sodium sand in 25 ml of refluxing toluene (under nitrogen) was added 2 ml of chlorotrimethylsilane. Then 0.20 ml of dimethyl 4,5-dimethylcyclohex-4-ene-cis-1,2-dicarboxylate was added over a period of 10 minutes. After refluxing an additional 4.5 hours (3 ml additional chlorotrimethylsilane being added in 1 ml portions at regular intervals throughout this period), the suspension was filtered and the solvent was removed at reduced pressure. An analytical sample of 4,5-dimethyl-7,8-bis(trimethylsiloxy)-bicyclo[4.2.0]octa-3,7-diene was obtained by preparative glpc (15% Carbowax 20 M, 160°).

NMR (CCl_4) δ0.15 (s, 18H), δ1.62 (s, 6H), δ1.85-2.05

(multiplet, 4H), δ2.42-2.60 (multiplet, 2H).

Dimethyl cis-1-methylcyclohex-4-ene-1,2-dicarboxylate

To a solution of 17.0 g of citraconic anhydride (Aldrich Chemical Co.) in 100 ml of dry benzene was added 25 g of 1,3-butadiene and the mixture was heated in a sealed glass bomb for 4 hours at 130°. The solvent and excess butadiene were removed at reduced pressure. Vacuum distillation gave 13.3 g of recovered citraconic anhydride, bp 73-77° at 4 mm, followed by 5.5 g of cis-1-methylcyclohex-4-ene-1,2-dicarboxylic anhydride, bp 114-119° at 4 mm (lit (117) bp 113-115° at 4 mm). This anhydride was refluxed with methanol and a trace of sulfuric acid for 5 hours. Normal workup and preparative glpc (15% Carbowax 20 M, 155°) gave pure dimethyl cis-1-methylcyclohex-4-ene-1,2-dicarboxylate.

Infrared (CCl_4) 1740 (C=O), 1650 (C=C), 1435, 1195, 1175 cm^{-1} (methyl ester).

NMR (CCl_4) δ1.18 (s, 3H), δ1.7-3.0 (multiplet, 5H), δ3.58 (s, 3H), δ3.61 (s, 3H), δ5.53 (broad singlet, 2H).

Mass Spec Mol wt 212; found M^+ = 212, prominent peaks at 181 (M-31), 180 (M-32), 153 (M-59).

cis-1-Methyl-7,8-bis(trimethylsiloxy)bicyclo[4.2.0]octa-3,7-diene (XCVa)

To 0.3 g of sodium sand in 25 ml of refluxing toluene (under nitrogen) was added 2 ml of chlorotrimethylsilane

followed by the addition of 0.20 ml of pure dimethyl cis-1-methylcyclohex-4-ene-1,2-dicarboxylate over a 10 minute period. After refluxing an additional 4.5 hours (3 ml of additional chlorotrimethylsilane being added in 1 ml portions at regular intervals throughout this period), the suspension was cooled, filtered and the solvent was removed at reduced pressure. An analytical sample of cis-1-methyl-7,8-bis(trimethylsiloxy)bicyclo[4.2.0]octa-3,7-diene (26) was obtained by preparative glpc (15% Carbowax 20 M, 160°).

NMR (CCl_4) δ0.15 (s, 18H), δ1.13 (s, 3H), δ1.75-2.20 (multiplet, 5H), δ5.50-5.67 (multiplet, 2H).

Dimethyl trans-1-methylcyclohex-4-ene-1,2-dicarboxylate

To a solution of 4.2 g of mesaconic acid (Aldrich Chemical Co.) in 25 ml of dioxane was added 10 g of 1,3-butadiene. This mixture was heated in a sealed tube at 135° for 2 hours followed by heating at 165° for 3 hours. The volatile materials were removed at reduced pressure. After repeated recrystallization from ethyl acetate-hexane, 1.5 g of trans-1-methylcyclohex-4-ene-1,2-dicarboxylic acid was obtained, mp 179-181° (lit (117) mp 180-181°). Esterification of this diacid (0.9 g) was effected by refluxing with methanol (20 ml) and a trace of sulfuric acid (0.2 ml) for 14 hours. Normal workup gave 0.7 g of dimethyl trans-1-methylcyclohex-4-ene-1,2-dicarboxylate. An analytical sample was obtained by preparative glpc (15% Carbowax 20 M, 160°).

NMR (CCl_4) δ1.20 (s, 3H), δ2.0-2.4 (multiplet, 4H), δ2.8-3.1 (multiplet, 1H), δ3.60 (s, 3H), δ3.62 (s, 3H), 5.55-5.68 (multiplet, 2H).

Mass Spec Mol wt 212; found M^+ = 212, prominent peaks at 181 (M-31), 153 (M-59), 152 (M-60).

trans-1-Methyl-7,8-bis(trimethylsiloxy)bicyclo[4.2.0]octa-3,7-diene (XCVIIa)

To a suspension of 0.8 ml sodium-potassium alloy (1:3) in 25 ml dry ether at 0° was added 1.0 ml of chlorotrimethylsilane and 0.050 ml of dimethyl trans-1-methylcyclohex-4-ene-1,2-dicarboxylate. After stirring at 0° (under nitrogen) for 3.5 hours, the solution was filtered and the solvent was removed in vacuo. Since the product, trans-1-methyl-7,8-bis(trimethylsiloxy)bicyclo[4.2.0]octa-3,7-diene (26), is reported to be thermally unstable, it was not further purified.

1-Methyl-2,3-bis(trimethylsiloxy)-1,3,6-cyclooctatriene (XCVIIIa)

To a suspension of 0.5 g sodium sand in 25 ml of refluxing toluene (under nitrogen) was added 2.0 ml of chlorotrimethylsilane and 0.15 ml of dimethyl trans-1-methylcyclohex-4-ene-1,2-dicarboxylate was added over a period of 15 minutes. After refluxing for 5 hours, the solution was cooled, filtered, and the solvent was removed at reduced pressure. An analytical sample of 1-methyl-2,3-bis(trimethylsiloxy)-1,3,6-cyclooctatriene (26) was obtained by

preparative glpc (15% Carbowax 20 M, 160°).

NMR (CCl_4) δ0.16 (s, 18H), δ1.63 (s, 3H), δ2.5-2.8 (multiplet, 4H), δ4.69 (t, J= 8 Hz,1H), δ5.4-5.6 (multiplet, 2H).

cis-1,2-Bis(carbomethoxymethyl)cyclobutane

A 3.0 g sample of cis-1,2-cyclobutanedicarboxylic anhydride (Aldrich Chemical Co.) was refluxed in 25 ml of water for 30 minutes. After cooling and filtering, 3.2 g of cis-1,2-cyclobutanedicarboxylic acid was obtained, mp 127-130° (lit (113) mp 139-140°). To 40 ml of dry benzene at 0° was added 10 ml of thionyl chloride, 10 drops of pyridine, and 3.2 g of cis-1,2-cyclobutanedicarboxylic acid. After stirring at room temperature for 20 hours, the benzene was removed at reduced pressure. The residue was dissolved in 100 ml of dry ether, filtered, and added dropwise to diazomethane (from 20 g Diazald) in 300 ml of ether over a period of 45 minutes. The solution was allowed to stand at room temperature for 20 hours. The ether was then removed at reduced pressure, the residue was dissolved in 70 ml of methanol and the solution was stirred under nitrogen while a solution of 0.5 g silver benzoate in 5 ml of dry triethyl amine was added over a period of 30 minutes. After stirring at room temperature for 2 hours, the solution was refluxed for 1 hour. After cooling and filtering, the methanol was removed in vacuo and the residue was dissolved in 200 ml of

ether. The ethereal solution was washed with 2N hydrochloric acid (3 x 40 ml), saturated sodium bicarbonate solution (3 x 40 ml) and saturated sodium chloride solution (40 ml). After drying over magnesium sulfate, the ether was removed at reduced pressure, leaving 2.1 g of crude product. Vacuum distillation gave 1.0 g of a colorless liquid bp 80-85° at 0.2 mm. An analytical sample of cis-1,2-bis(carbomethoxymethyl)-cyclobutane (118) was obtained by preparative glpc (15% Carbowax 20 M, 150°).

Infrared (CCl_4) 1740 (C=O), 1435, 1350, 1190, 1165 cm^{-1} (methyl ester).

NMR (CCl_4) δ1.5-3.0 (multiplet, 10H), δ3.60 (s, 6H).

Mass Spec Mol wt 200; found M^+ = 200, prominent peaks at 168 (M-32), 141 (M-59).

Di-t-butyl-1,2-diazetidinedione (XCIXa)

This diketone was prepared by the method of Stowell (55); mp 55-57° (lit (55) mp 56-57°). Spectral data were consistent with the reported values.

2,3-Dicarboethoxy-2,3-diazabicyclo[2.2.1]heptane (Ca)

2,3-Dicarboethoxy-2,3-diazabicyclo[2.2.1]heptane was prepared by the method of Cohen, Zand and Steel (119)

NMR (CCl_4) δ1.25 (t, J = 7 Hz, 6H), δ1.60 (s, 2H), δ1.72 (s, 4H), δ4.11 (q, J = 7 Hz, 4H), δ4.48 (s, 2H).

Dimethyl 7-oxabicyclo[2.2.1]hept-5-ene-exo, exo-2,3-dicarboxylate (CXIb)

A solution of 14.0 g of maleic anhydride and 9.0 g of furan in 50 ml of chloroform was allowed to stand at room temperature for 10 hours. Upon filtration, 11.1 g of 7-oxabicyclo[2.2.1]hept-5-ene-exo, exo-2,3-dicarboxylic anhydride was obtained, mp 110-112° (lit (120) mp 125°). Esterification with methanol and a trace of sulfuric acid (refluxed 4.5 hours) gave dimethyl-7-oxabicyclo[2.2.1]hept-5-ene-exo, exo-2,3-dicarboxylate, mp 117-119° (lit (121) mp 119°).

NMR ($CDCl_3$) δ2.80 (s, 2H), δ3.68 (s, 6H), δ5.22 (t, J = 1 Hz, 2H), δ6.45 (t, J = 1 Hz, 2H).

Dimethyl cis-7,8-dimethylbicyclo[4.2.0]octane-7,8-dicarboxylate (CVa)

To a solution of 3.0 g of dimethylmaleic anhydride in 85 ml of cyclohexene was added 2.0 g benzophenone. After degassing with nitrogen for 1 hour, the solution was irradiated at 3500Å for 7 days at about 50°. The cyclohexene was removed by distillation and the residue was dissolved in 200 ml of ether. After adding 200 ml of pentane, the solution was cooled to -20°. Filtration gave 3.0 g of white crystals. Sublimation (60° at 0.4 mm) followed by recrystallization from hexane gave 2.5 g of cis-7,8-dimethylbicyclo[4.2.0]-octane-7,8-dicarboxylic anhydride, mp 68-70° (lit (122) mp 66-68°). A 0.5 g sample of this anhydride was refluxed in

1.5 ml of pure methanol for 10 hours. The excess methanol was removed, the residue was dissolved in 20 ml of ether and reacted with diazomethane (from 1.5 g Diazald) in 25 ml of ether. After standing at room temperature for 2 hours, the solution was diluted to 100 ml with ether, extracted with 10% sodium hydroxide (15 ml) and saturated sodium chloride solution (2 x 15 ml), and dried over magnesium sulfate. Evaporation of the ether followed by preparative glpc (15% Carbowax 20 M, 190°) gave dimethyl cis-7,8-dimethylbicyclo-[4.2.0]octane-7,8-dicarboxylate (presumably a mixture of about equal parts of the two stereoisomers based upon the NMR spectrum).

Infrared (CCl_4) 1730 (C=O), 1460, 1445, 1430, 1190, 1150 1135 cm^{-1}.

NMR (CCl_4) δ1.20 (s, 3H), δ1.25 (s, 3H), δ1.2-2.5 (multiplet, 10H), δ3.57 (s, 3H), δ3.62 (s, 3H).

Mass Spec Mol wt 254; found M^+ = 254, prominent peaks at 223 (M-31), 222 (M-32), 195 (M-59).

Dimethyl bicyclo[2.1.0]pentane-endo, endo-2,5-dicarboxylate (CXIIa)

7-Chloronorbornadiene (Frinton Laboratories) was reduced with lithium aluminum hydride in ether by the method of Story (123) to a mixture of tricyclo[2.2.1.$0^{6,7}$]hept-2-ene (123, 124) and norbornadiene. Due to the instability of the desired tricyclic olefin and the difficulty of separating

it from the norbornadiene, the crude reaction product was ozonized. A mixture of ozone in oxygen was passed through a solution of 2.0 g of the crude product in 50 ml of methanol at -75° until the purple color persisted in solution. The methanol was removed at reduced pressure and the residue was dissolved in 25 ml of 90% formic acid. When 15 ml of 30% hydrogen peroxide was added an exothermic reaction took place. The solution was stirred at ambient temperatures for 40 minutes, then refluxed for 30 minutes. After cooling, the solvent was removed in vacuo. The residue was dissolved in 200 ml of ether, dried over magnesium sulfate and concentrated to 50 ml. To this solution was added a solution of diazomethane (from 16.0 g Diazald) in 200 ml ether. After standing at room temperature for 16 hours the excess diazomethane was destroyed by adding acetic acid. The ethereal solution was washed with saturated sodium bicarbonate solution (2 x 20 ml) and saturated sodium chloride solution (20 ml). After drying over magnesium sulfate, the ether was removed at reduced pressure, leaving 1.7 g of a light yellow liquid. An analytical sample of dimethyl bicyclo[2.1.0]-pentane-endo, endo-2,5-dicarboxylate was obtained by preparative glpc (15% Carbowax 20 M, 180°).

Infrared (neat) 3060 (cyclopropane), 1728 cm^{-1} (C=O).

NMR (CCl_4) δ1.66 (t, J = 6 Hz, 1H), δ1.9-2.6 (multiplet, 4H), δ3.1-3.4 (multiplet, 1H), δ3.52 (s, 3H),

δ3.61 (s, 3H).

Mass Spec Mol wt 184; found M^+ = 184, prominent peaks at 153 (M-31), 125 (M-59).

Tricyclo[2.2.2.$0^{2,6}$]octan-7,8-dione (CXIVa)

A mixture of tricyclo[2.2.2.$0^{2,6}$]octan-7-one and tricyclo-[2.2.2.$0^{2,6}$]octan-8-one was prepared by the method of Lumb and Whitham (125). To a solution of 1.0 g (0.008 mole) of the mixture of ketones in 15 ml of 95% ethanol was added 1.0 g (0.009 mole) selenium dioxide and the mixture was refluxed for 5 hours. The solvent was removed at reduced pressure and the residue was dissolved in 100 ml ether. To this solution was added 2.0 g of freshly precipitated silver metal and the mixture was refluxed for 3 hours. After filtration, the ether was removed *in vacuo* and the residue was sublimed (80° at 0.05 mm) to give 470 mg (42%) of a yellow solid. After recrystallization from benzene-hexane, the yellow crystals melted at 153-155°.

Infrared (KBr) 1740, 1705, 1690 (), 1320, 1312, 1260, 1004, 960, 930, 852, 792, 750 cm^{-1}.

NMR ($CDCl_3$) δ2.0-2.5 (multiplet, 7H), δ2.85-3.05 (multiplet, 1H).

Mass Spec Mol wt 136; found M^+ = 136, prominent peaks at 108 (M-28), 80 (M-56), 79 (M-57), 77 (M-59).

Dimethyl endo-3-syn-6-bicyclo[3.1.0]hexane dicarboxylate (CXIVb)

Tricyclo[2.2.2.$0^{2,6}$]oct-7-ene was prepared by the method of Grob and Hostynek (126). An analytical sample was obtained by preparative glpc (15% Carbowax 20 M, 70°). Ozone was bubbled into a solution of 90 mg of this olefin in 10 ml of methanol at -75° until the purple color persisted. The methanol was evaporated at reduced pressure. To the residue was added 3 ml of 90% formic acid and 1.0 ml of 30% hydrogen peroxide. After stirring at ambient temperatures for 30 minutes, the solution was refluxed for 30 minutes. After cooling, the solvent was removed in vacuo, leaving a white crystalline paste. This residue was taken up in 25 ml of ether and reacted with diazomethane (from 2.5 g Diazald) in 40 ml of ether. The excess diazomethane was destroyed with acetic acid. After washing the ethereal solution with saturated sodium bicarbonate solution and saturated sodium chloride solution, it was dried over magnesium sulfate and the ether was carefully distilled off. An analytical sample of dimethyl endo-3-syn-6-bicyclo[3.1.0]hexane dicarboxylate was obtained by preparative glpc (15% Carbowax 20 M, 180°).

Infrared (neat) 3050 (cyclopropane), 1725 cm^{-1} (C=O).

NMR (CCl_4) δ1.60-2.35 (multiplet, 7H), δ2.90-3.40 (multiplet, 1H), δ3.60 (s, 6H).

Mass Spec Mol wt 198; found M^+ = 198, prominent peaks at

167 (M-31), 166 (M-32), 139 (M-59), 138 (M-60), 107 (M-91), 79 (M-119).

2-Methyl 4,5,6,7-tetrahydroindan-1-one (CXXXIVa)

To 250 g of polyphosphoric acid (FMC Corporation) maintained at about 55° and rapidly stirred under a nitrogen atmosphere was added a mixture of 17.2 g methacrylic acid and 16.4 g of cyclohexene. After stirring for 45 minutes, the reddish-brown complex was decomposed in ice water (500 ml). To the solution was added 150 g of ammonium sulfate and this solution was thoroughly extracted with hexane (5 x 100 ml). The organic extract was washed with water (50 ml), 5% ammonium hydroxide (3 x 50 ml) and saturated sodium chloride solution (2 x 50 ml). The organic phase was dried over magnesium sulfate and the solvent was removed at reduced pressure. Vacuum distillation gave 6.6 g of 2-methyl 4,5,6,7-tetrahydroindan-1-one, bp 96-98° at 4 mm.

Infrared (CCl_4) 1700 (C=O), 1650 cm^{-1} (C=C).

NMR (CCl_4) δ1.10 (d, J = 7 Hz, 3H), δ1.40-3.00 (multiplet, 11H).

Mass Spec Mol wt 150; found M^+ = 150.

Derivative 2,4-Dinitrophenylhydrazone, mp 231-232°.

2,3-Dihydroxycymene

2,3-Dihydroxycymene was prepared by the procedure of Treibs and Albrecht (127).

Dimethyl 1,4-diphenylpiperazine-2,3-dicarboxylate

A mixture of *cis* and *trans* dimethyl 1,4-diphenylpiperazine-2,3-dicarboxylate was prepared by the method of Huisgen, Scheer and Szeimies (128). Spectral data were consistent with published values. The two isomers were partially separated by column chromatography on silica gel.

Electron Spin Resonance Studies

The ESR spectra were obtained using either a Varian V-4500 spectrometer equipped with 100 kHz field modulation and a 9 inch magnet or a Varian E-3 spectrometer equipped with a 4 inch magnet and 100 kHz field modulation. Flat fused silica cells (Varian V-4548 aqueous solution sample cell) were used in conjunction with the previously described (129) inverted U-type mixing cells.

Oxidation of ketones with an α-methylene group was carried out essentially as described previously (4, 130). Solutions of the ketone (0.1-0.2 M) and potassium t-butoxide (0.2-0.6 M) in DMSO (equal volumes) were placed in separate legs of the inverted U-type mixing cell, the solutions were purged with prepurified nitrogen for 15-20 minutes, the cell was stoppered and the solutions were mixed. Air was admitted to the solution for 5-10 seconds and the contents of the cell were well mixed by shaking. If the desired radical was not observed after about 30 minutes, air was admitted again for 5 seconds, this process being repeated if necessary.

Reduction of α-diketones to semidiones was accomplished by mixing a well deoxygenated solution of the diketone (about 0.1 M) and propiophenone (about 0.04 M) in DMSO with an equal volume of a deoxygenated solution of potassium t-butoxide (about 0.2 M) in DMSO (12), or by reaction of a deoxygenated solution of the diketone (about 0.1 M) in DME with an excess

of sodium-potassium alloy.

The *in situ* acyloin condensations were carried out by mixing a deoxygenated solution of the diester (0.4 M) in DME with a suspension of sodium-potassium alloy (1:1) in an equal volume of deoxygenated DME (about 120 mg of alloy per 1 ml of DME) and shaking for about 1 minute. If the signal was very weak, the solution was vigorously shaken again. In cases where extreme line broadening occurred, removing an aliquot of the solution (no sodium-potassium alloy being transferred) and mixing it with an equal volume of deoxygenated solution of potassium *t*-butoxide (0.2 M) in DMSO usually gave a better resolved spectrum. The admission of air to the solution for 5 seconds often further improved the quality of the ESR spectrum.

Semidiones were prepared from bis(trimethylsiloxy)alkenes by simply mixing equal volumes of well deoxygenated solutions of the bis(trimethylsiloxy)alkene (0.2 M) and potassium-*t*-butoxide (0.4 M) in DMSO. The reactions were usually carried out on a semimicro scale. To a suspension of 0.2 ml of sodium-potassium alloy (1:3) in 25 ml of ethyl ether at 0° (under nitrogen) was added 1 ml of chlorotrimethylsilane followed by 0.1-0.2 mmole of the pure diester. After stirring vigorously under nitrogen for 1-3 hours (time depending upon the ease of cyclization and the expected stability of the product), the suspension was filtered, the ether was removed

in vacuo and the residue was taken up in 0.5 ml of DMSO. This solution was deoxygenated and mixed with 0.5 ml of a deoxygenated solution of potassium *t*-butoxide (0.4 M) in DMSO in the ESR cell.

SOURCES OF CHEMICALS

Chemical	Source
Dimethyl sulfoxide	Baker, Mallinckrodt
Calcium hydride	Metal Hydrides, Inc.
Potassium t-butoxide	MSA Research Corp.
Cesium t-butoxide	MSA Research Corp.
Hexadeuteriodimethyl sulfoxide	Fluka, Mallinckrodt
Chlorotrimethylsilane	Aldrich
Diazald	Aldrich
Selenium dioxide	Alpha Inorganics
Isophorone	Aldrich
2-Butyne	Chemical Samples Co.
Dimethyl succinate	Aldrich
Dimethyl glutarate	Aldrich
Dimethyl pimelate	Aldrich
Dimethyl adipate	Aldrich
Thujone	Fluka
Diethyl cis-1,4-cyclohexane-dicarboxylate	Eastman Organic Chemicals
Diethyl cis-1,3-cyclohexane-dicarboxylate	Dr. E. T. Sabourin
Diethyl cis-1,2-cyclohexane-dicarboxylate	Dr. E. T. Sabourin
β-Dihydroumbellulone	Dr. R. H. Eastman
Nortricyclanone	Dr. J. J. McDonnell
1,3-Cycloheptadiene	Mr. R. G. Keske

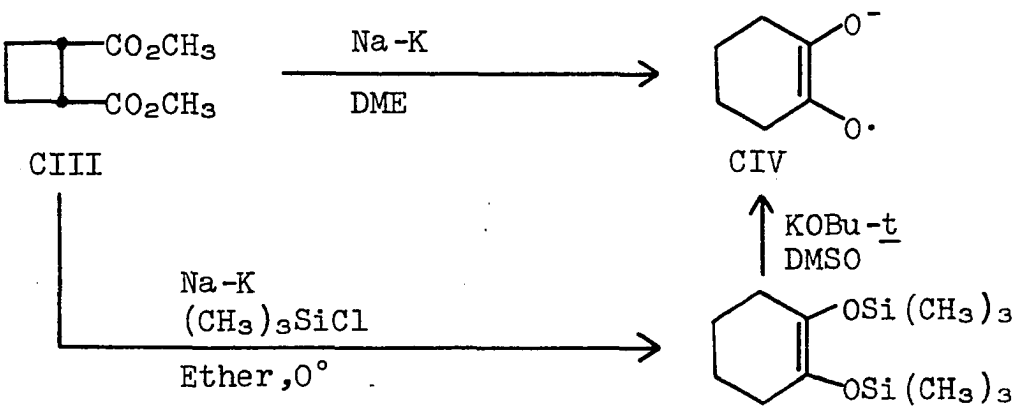
Chemical	Source
7-Chloronorbornadiene	Frinton Laboratories
Bicyclo[3.3.0]oct-1(5)-en-2-one	Badische Anilin-und Soda-Fabrik
Bicyclo[3.2.0]heptan-2-one	Dr. W. J. Hammar
1-Methylbicyclo[4.1.0]heptan-2-one	Dr. J. B. Stothers
6-Methylbicyclo[4.1.0]heptan-2-one	Dr. J. B. Stothers
4,6-Dimethylbicyclo[4.1.0]heptan-2-one	Dr. J. B. Stothers
1,4,4-Trimethylbicyclo[3.2.0]-heptan-2-one	Dr. O. L. Chapman
1,4,4-Trimethylbicyclo[3.2.0]hept-6-en-2-one	Dr. O. L. Chapman
Lumiisocolchicine ketol	Dr. O. L. Chapman
β-Lumicolchicine	Dr. O. L. Chapman
endo, endo-2,3-Bicyclo[2.2.2]-octanedicarboxylic acid	Mr. G. W. Holland
Dimethyl 5-norbornene-endo, endo-2,3-dicarboxylate	Mr. G. W. Holland
Dimethyl 5-norbornene-exo, exo-2,3-dicarboxylate	Mr. G. W. Holland
syn-Bicyclo[3.1.0]hexan-2-one-6-spiro-1'(2',2'-dimethyl-cyclopentane)	Dr. D. I. Schuster
cis-10β-Methyl-7α-isopropyl-2-n-butylthiomethylene-1-decalone	Dr. J. A. Marshall
9β,10β-Dimethyl-7α-isopropyl-3-octal-2-one	Dr. J. A. Marshall
12-Hydroxytricyclo[4.4.2.0]dodeca-3,8-dien-11-one	Dr. J. J. Bloomfield

Chemical	Source
1,5-Dicarbomethoxytetracyclo-[3.2.0.$0^{2,7}$.$0^{4,6}$]heptane	Dr. H. Prinzbach
1,5-Dicarbomethoxy-3-oxo-tetracyclo[3.2.0.$0^{2,7}$.$0^{4,6}$]heptane	Dr. H. Prinzbach
4,5-Dimethylcyclohex-4-ene-*cis*-1,2-dicarboxylic anhydride	Mr. G. W. Holland

APPENDICES

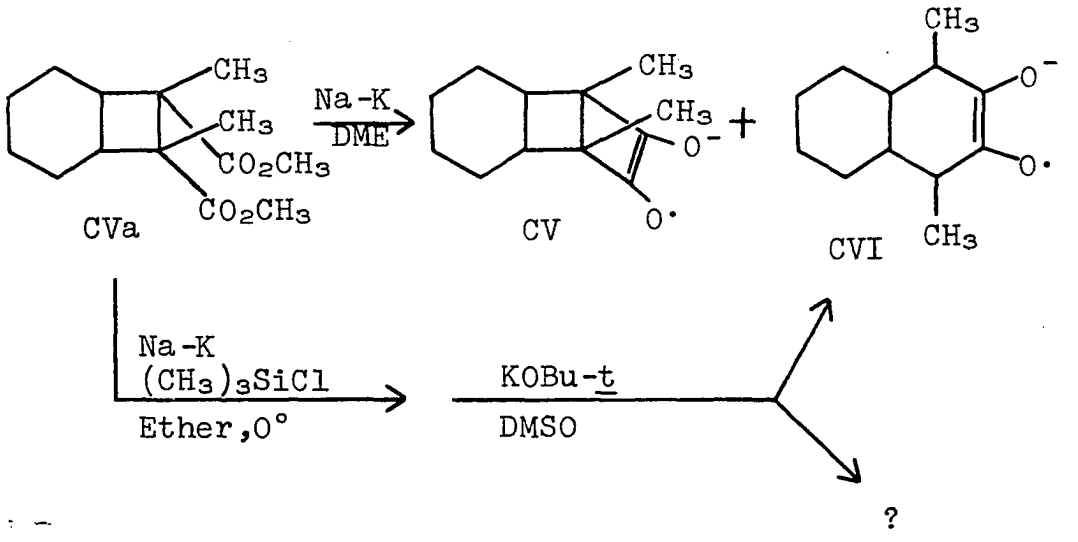
Ring Opening Reactions and Rearrangements Under Acyloin Conditions

Reaction of dimethyl cis-1,2-cyclobutanedicarboxylate (CIII) with sodium-potassium alloy in DME gave a low concentration of a radical anion with the same hfsc as cyclohexanesemidione (CIV) (Figure 83a; a^H = 10.1 (4H) gauss; see Table 1). Likewise, when the acyloin condensation was

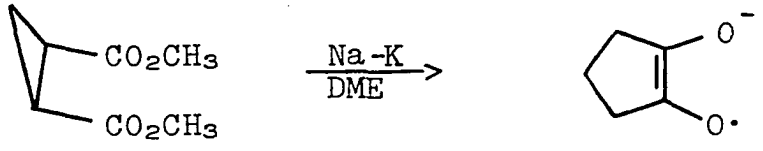


carried out in ether in the presence of excess chlorotrimethylsilane and the crude product was reacted with potassium t-butoxide in DMSO, the same radical anion was observed (Figure 83b; a^H = 9.9 (4H) gauss). When the cyclobutane derivative CVa was reacted with sodium-potassium alloy in DME, the major radical which was observed (Figure 84a) had an ESR spectrum which was a broad singlet that could not be further resolved and could possibly be due to the substituted cyclobutanesemidione CV. The chlorotrimethylsilane trapping

technique gave a mixture of radicals, the major one believed to be CVI (Figure 84b; a^H = 12.5 (2H) gauss - remainder of hfsc not well resolved). Similarly, reaction of dimethyl



cis-1,2-cyclopropanedicarboxylate with sodium-potassium alloy in DME gave cyclopentanesemidione (Figure 85; a^H = 13.8 (4H) gauss; see Table 1).

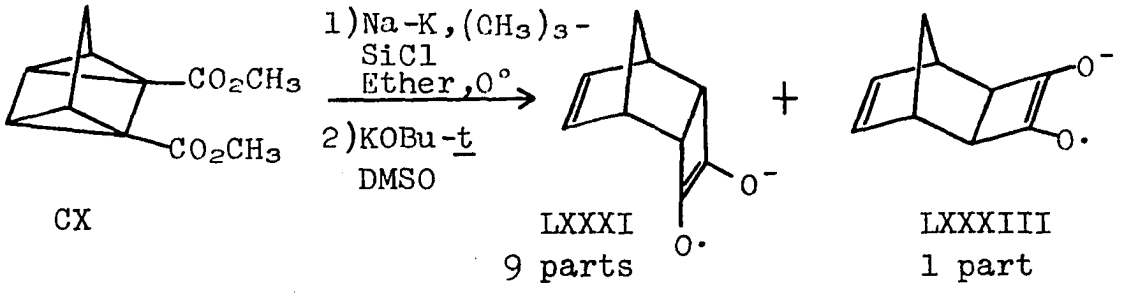


CVII CVIII

Bloomfield, Todd and Takahashi (131) found that diethyl cis-1,2-cyclobutanedicarboxylate reacted under acyloin conditions to give 2-carbethoxycyclopentanone as the major product (9-20% yield with sodium in refluxing toluene and 40% yield with sodium in liquid ammonia) with no acyloin products

isolated. Two mechanisms were discussed and are shown in Chart XIII. Abstraction of a proton from the solvent by CIXe to give diethyl adipate, followed by the acyloin condensation of this diester, could easily explain our results. Since the overall efficiency of this process is very low (probably much less than 1%), the acyloin would not be detected in a synthetic reaction. Since the anion of 2-carboethoxycyclopentanone would be stable under the reaction conditions and is diamagnetic, the observed ESR spectrum is remarkably clean. The somewhat surprising fact is that the reaction seems to be more facile in ether in the presence of chlorotrimethylsilane, a very good carbanion trapping agent. Since the carbanions involved are quite basic, perhaps proton abstraction from solvent is much more facile than nucleophilic attack upon chlorotrimethylsilane. This same type of mechanism could explain the formation of cyclopentanesemidione from dimethyl cis-1,2-cyclopropanedicarboxylate.

Another rearrangement of this general type which has been observed is the following:

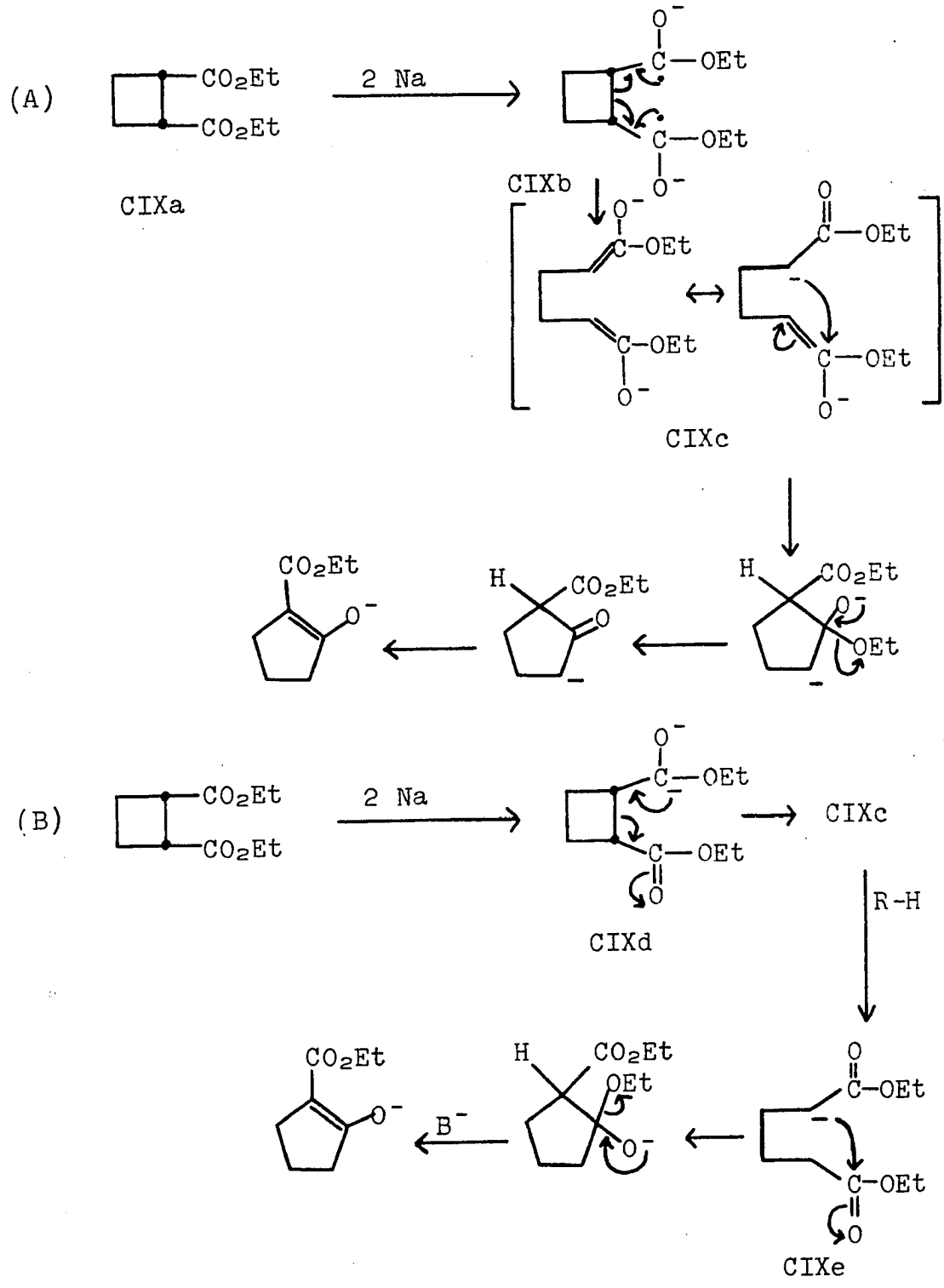


CX

LXXXI
9 parts

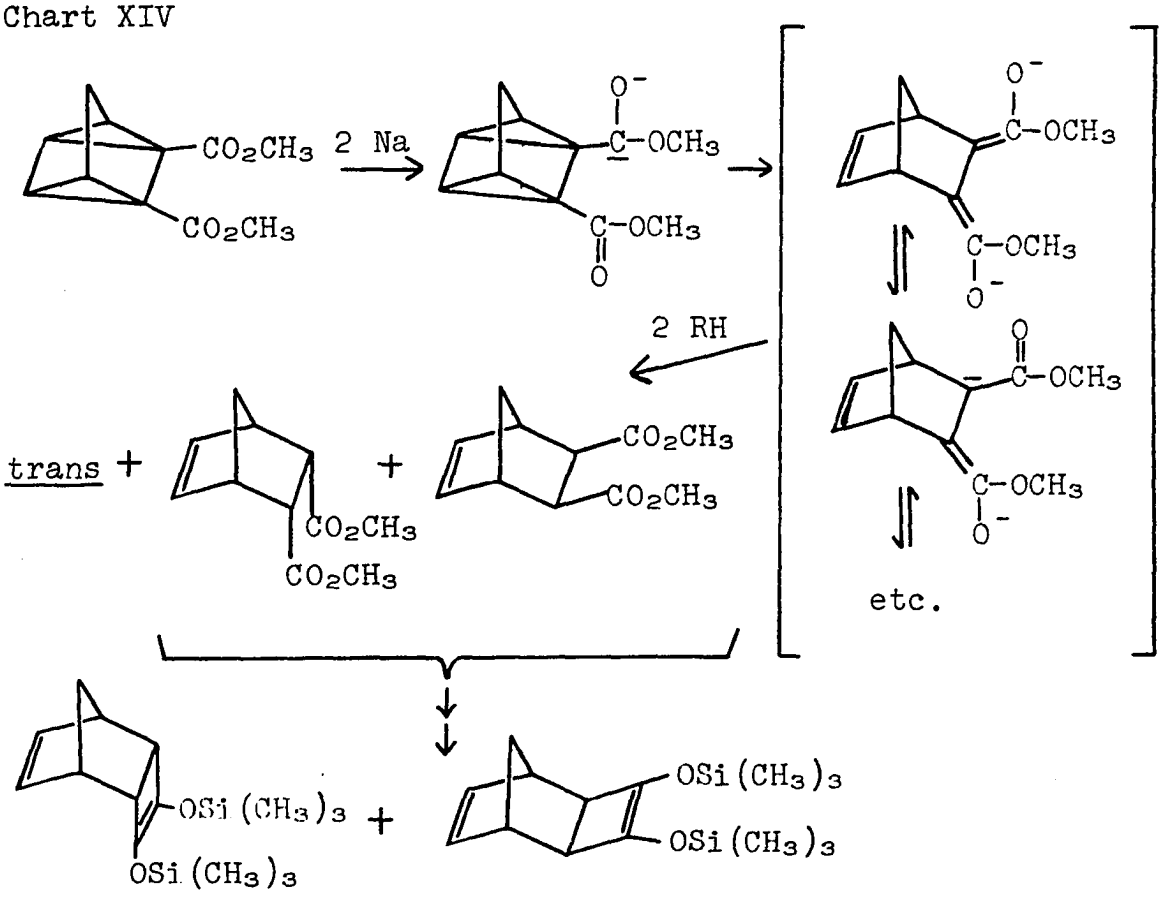
LXXXIII
1 part

Chart XIII


(A)
CO2Et
CO2Et
2 Na
OEt
CIXa
CIXb
CIXc
H
OEt
(B)
2 Na
CIXc
CIXd
R-H
B-
CIXe

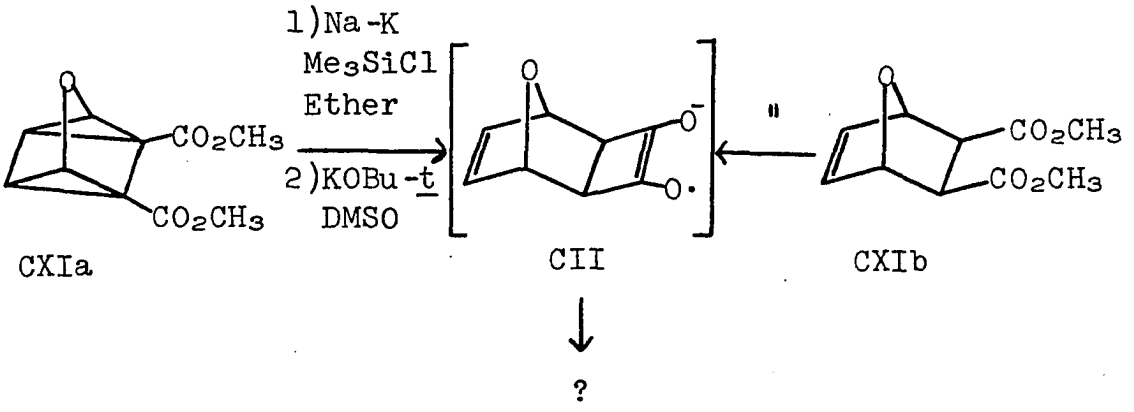
Both endo- and exo-tricyclo[4.2.1.$0^{2,5}$]non-7-ene-3,4-semidiones (discussed earlier) were observed in the approximate ratio of 9:1 (see Figure 86a). When the crude acyloin product was reacted with potassium t-butoxide in d_6-DMSO, very little hydrogen-deuterium exchange was observed (see Figure 86b), which demands that at least the major part of the rearrangement occurs during the acyloin condensation itself. A mechanism can be written for this rearrangement which is very similar to that proposed for the formation of cyclohexanesemidione from dimethyl cis-1,2-cyclobutanedicarboxylate and is shown in Chart XIV.

Chart XIV



The endo- diester would be expected to be the major product since R-H can enter more easily from the less hindered exo side of the molecule. Thus, we observe a 9:1 ratio of LXXXI to LXXXIII.

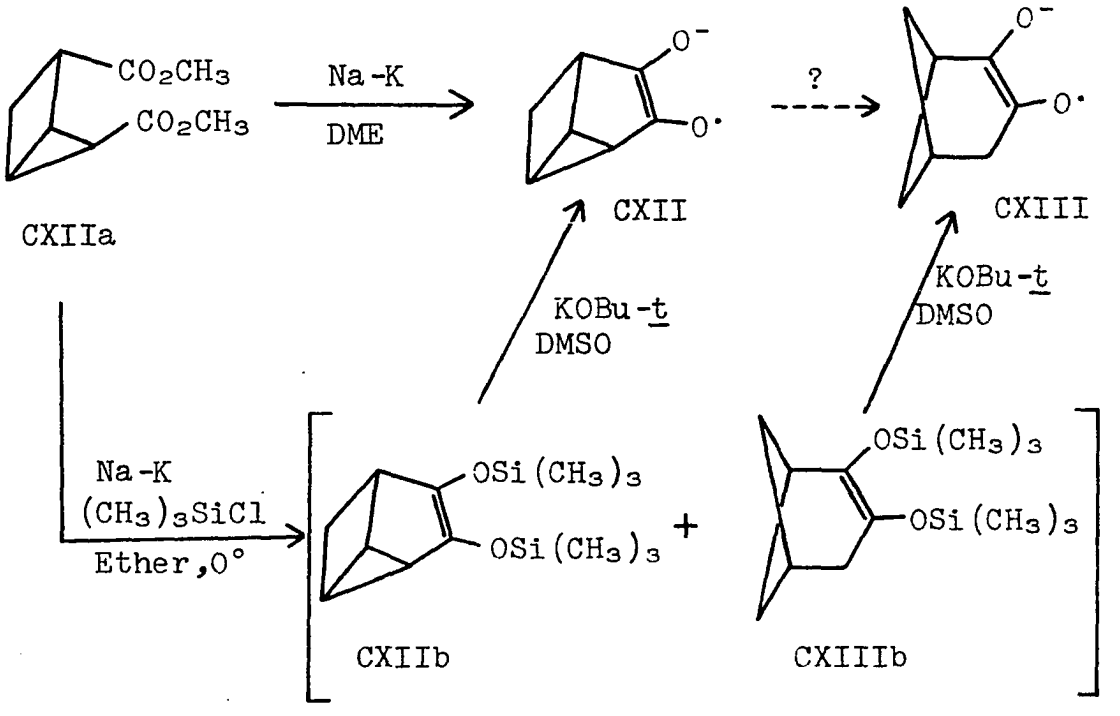
Under conditions similar to those described for CX, reaction of CXIa gave a radical anion (Figure 87; a^H = 2.7 (2H) and 0.4 (4H) gauss) whose structure is unknown, but is probably not CXI. The same radical anion is formed from CXIb.



Further work in this system will be required to solve this problem.

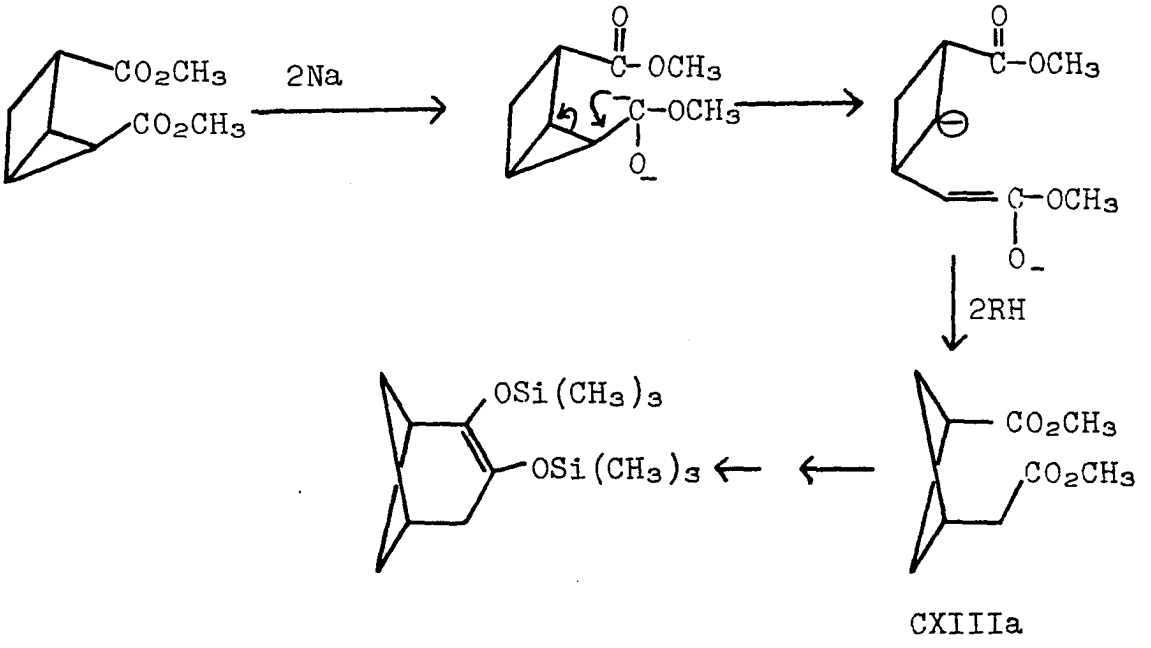
When dimethyl endo, endo-2,5-bicyclo[2.1.0]pentanedicarboxylate (CXIIa) was reacted with sodium-potassium alloy in DME, a single radical anion, presumably CXII, was produced (Figure 88; a^H = 11.7, 10.7, 3.4, 0.4 and 0.4 gauss). When the acyloin condensation was carried out in ether in the presence of chlorotrimethylsilane and the crude product was reacted with potassium t-butoxide in DMSO, a mixture of

two radicals was obtained (Figure 89a; radical A: a^H = 10.10 (2H), 3.50 (2H), 0.35 and 0.20 gauss; radical B: a^H = 9.95, 9.40, 3.60, 0.45, 0.35 and 0.15 gauss). Note that the pattern of the hfsc for radical B is the same as that for the radical observed in DME. Radical B decays much more rapidly than A so that after 2 hours, only radical A is observed (Figure 89b). The hfsc for radical A are identical to the hfsc observed in semidione CXIII[a].



[a]Keske, R. G., Department of Chemistry, Iowa State University, Ames, Iowa 50010. Predoctoral research at Iowa State University. Private communication. 1968.

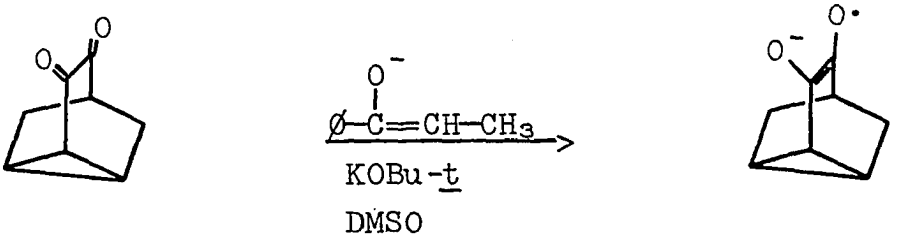
When the crude acyloin product was reacted with potassium t-butoxide in d_6-DMSO, the spectrum in Figure 90 was obtained (a^H = 3.50 (2H), 0.35 and 0.20 gauss; a^D = 1.55 (2D) gauss), which is consistent with CXIII with deuterium atoms at C-4. The other radical was not detected in this experiment. One can explain the formation of CXIIIb by the same type of mechanism as previously discussed, namely:



CXIIIa

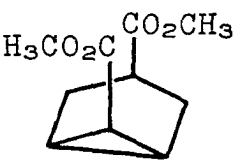
Alternatively, we cannot rule out the base catalyzed rearrangement of CXII to CXIII, which requires breaking the C_4-C_5 bond and gaining two hydrogen atoms.

Reduction of the diketone CXIVa with the enolate anion of propiophenone (12) in a solution of potassium t-butoxide in DMSO gave a single radical anion (Figure 91; a^H = 0.55 (2H) and 0.22 (2H) gauss) which was assigned to CXIV. On



CXIVa CXIV

the other hand, the chlorotrimethylsilane acyloin technique with CXIVb

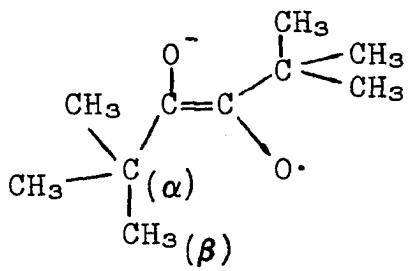


CXIVb

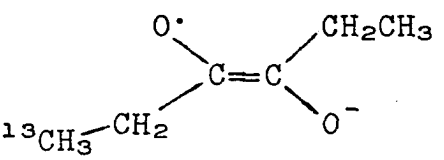
gave, in addition to the above radical, a mixture of two other minor radicals. After 1 hour, CXIV had essentially all decayed but the two other radicals remained (Figure 92; radical A: a^H = 4.15 (2H) and 0.15 (6H) gauss; radical B: a^H = 1.8 (4H, about equivalent) gauss). The structures of these radicals are unknown and further work would be necessary to delineate the nature of this rearrangement.

Carbon-13 Splitting in Rigid Polycyclic Semidiones

Carbon-13 coupling constants in semidiones have been discussed recently by Russell and Underwood (28) and by Malkus (132). In general, in acyclic semidiones, the carbonyl carbons have carbon-13 couplings in the range 0.5-1.5 gauss whereas the α-carbon couplings are in the range 3.5-6.2 gauss. The β-carbon couplings in CXV are 2.4 gauss (28) whereas the β-carbons in CXVI (in a sample in which the β-carbons are



CXV



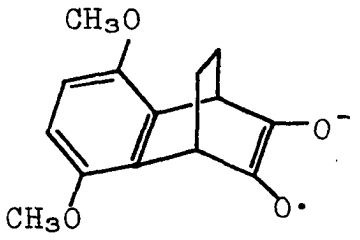
CXVI

enriched in carbon-13) have a coupling constant of 4.25 gauss.[a]

Due to the difficulty of selective incorporation of carbon-13 into bicyclic systems, little is known about ^{13}C hfsc in bicyclic semidiones. Only one ^{13}C coupling ($a^{^{13}C}$ = 6.15 gauss) was observed in the spectrum of CXVII (28) and was believed to be due to the α-carbons.

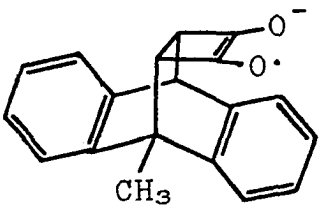
---

[a]Lawson, D. F., Department of Chemistry, Iowa State University, Ames, Iowa 50010. Predoctoral research at Iowa State University. Private communication. 1969.



CXVII

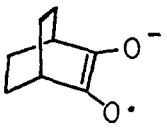
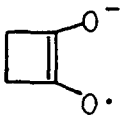
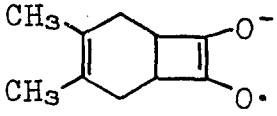
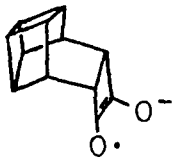
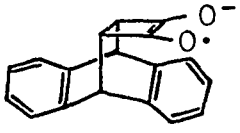
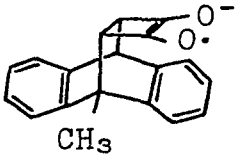
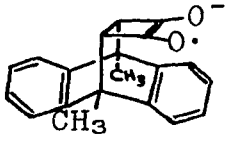
We have been able to observe ^{13}C couplings (natural abundance) in a few favorable cases. These results are shown in Table 5. The assignments in cyclobutanesemidione are based upon results for acyclic semidiones in which case the carbonyl carbons have the lower coupling constant. The other assignments are based upon an extension of these couplings. The very "fuzzy" multiplets associated with the largest carbon-13 coupling in Figure 98 are further evidence that the largest coupling is due to the β-carbons since in LXX, the



LXX

β-carbons are not expected to be magnetically equivalent. The very small difference in coupling constants of the two β-carbons leads to a less intense and broadened multiplet.

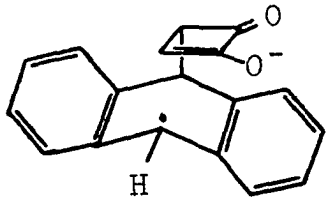
Table 5. Carbon-13 hyperfine splitting constants in DMSO solution at 25°

Semidione	$a^{13}C$ (gauss) $C_{C=O}$	C_{α}	C_{β}	Figure
	?[a]	?[a]	7.6	93
	1.4	5.4	---	94
	1.5	5.0	7.9	95
	1.4	4.9	9.2	96
	1.1	5.1	8.7	97
	-[b]	5.1	8.7	98
	-[b]	5.1	8.6	99

[a]Another splitting is observed ($a^{13}C$ = 1.8 gauss) which is due to 2 carbons but cannot be assigned with certainty.

[b]Cannot be measured due to the linewidth of the ^{12}C spectrum lines.

It can be noted from Table 5 that the carbon-13 coupling constants are reasonably constant throughout the series. The β-carbon couplings must be due primarily to a carbon-carbon hyperconjugation mechanism as in LXVIIIa, since if only spin polarization were involved, the β-carbon splitting should be

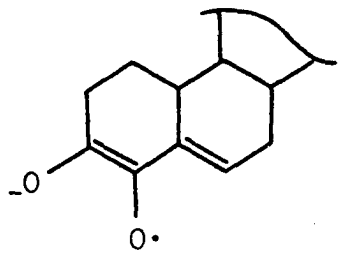


LXVIIIa

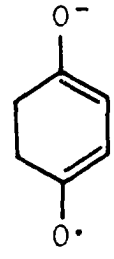
less than that of the α-carbon (spin polarization decreases by about a factor of three for each bond involved). Since the β-couplings are rather constant, carbon-carbon hyperconjugation must occur to about an equal extent in each of the cases.

Semidiones from α,β-Unsaturated Ketones

A large volume of information concerning semidiones has been assimilated over the past five years. However, very little is known about semidiones which are conjugated with a double bond. A few examples of this type (CXVIII) were observed in steroids (6) and conjugated radical anions of the type CXIX (a^H = 5.79 (2H) and 2.35 (4H) gauss) have been detected (6). However, a systematic study of conjugated semidiones has not been undertaken.



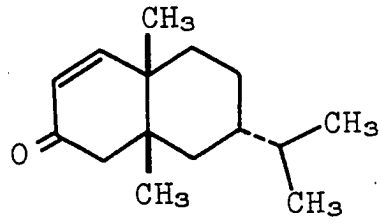
CXVIII



CXIX

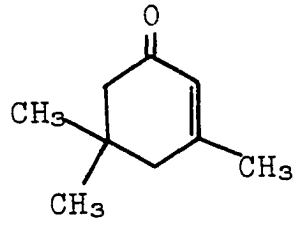
We have studied the reactions of a few α,β-unsaturated ketones with potassium t-butoxide and oxygen in DMSO. The starting enones and the observed hfsc are shown in Chart XV.

Chart XV



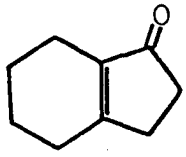
CXXa

a^H = 5.45 G
1.75 G



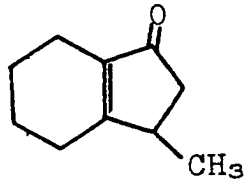
CXXIa

a^H = 5.40 G (3H)
4.75 G
1.75 G (2H)



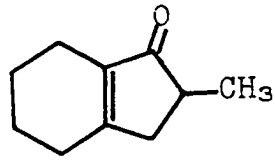
CXXIIa

a^H = 9.90 G (2H)
7.10 G (2H)
4.20 G (2H)
0.25 G (2H)



CXXIIIa

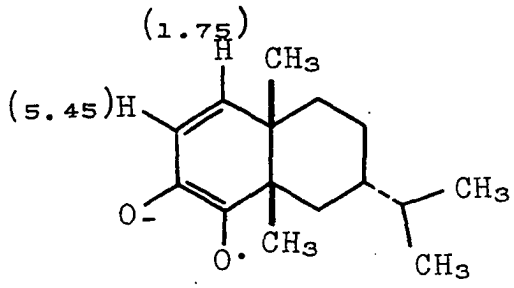
a^H = 9.80 G
9.60 G
7.50 G
6.10 G
3.50 G
0.25 G (2H)



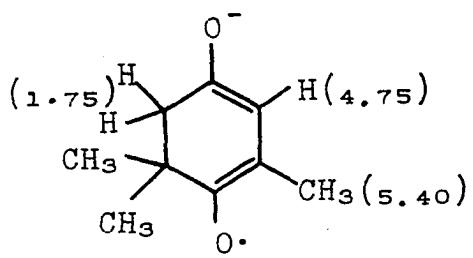
CXXIVa

a^H = 9.85 G
9.70 G
6.40 G
4.40 G
3.75 G
0.25 G (5H)

The semidione derived from CXXa (Figure 100) must have the structure shown in CXX with coupling by both vinyl hydrogens. On the other hand, CXXIa is oxidized at C-4 to yield



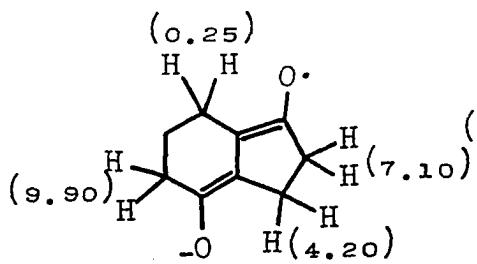
CXX



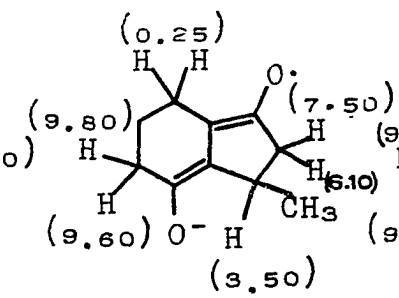
CXXI

the conjugated radical anion CXXI (Figure 101). Note that the hfsc in CXXI are very similar to those reported for CXIX.

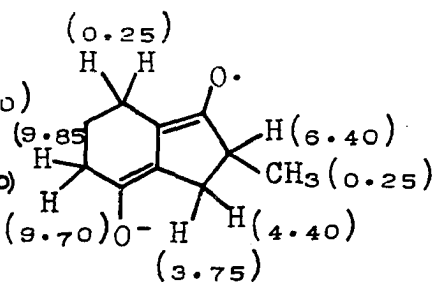
A comparison of the hfsc for the radical anions obtained from CXXIIa-CXXIVa shows that the same type of structure is involved in each case. (Minor radicals are formed in each case, but their ESR spectra cannot be resolved--see Figures 102-104). The hfsc seem most consistent with the structures shown in CXXII-CXXIV. The assignment of the hfsc to given



CXXII

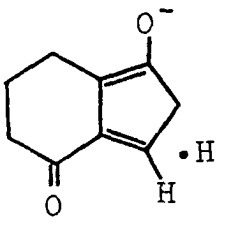


CXXIII

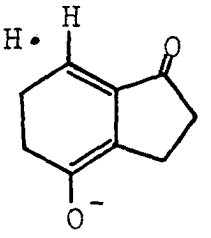


CXXIV

hydrogens is based upon the size of the coupling eliminated by the introduction of a methyl group at that position. If this assignment is correct, the much larger coupling (about 4 gauss) of the C-9 hydrogens than the C-5 hydrogens (0.25 gauss) must mean that hyperconjugation structure CXXIIb is much more important than CXXIIc.

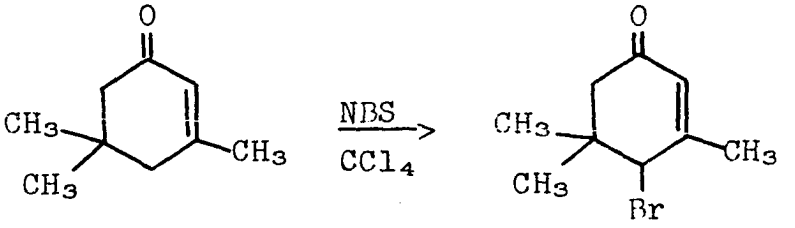


CXXIIb



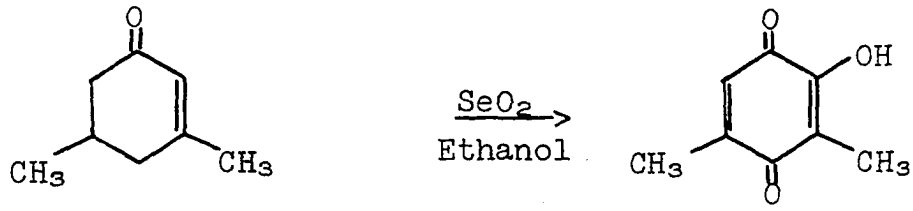
CXXIIc

The observed oxidation mode of isophorone (CXXIa) is similar to other reactions of this type of enone. Its reaction with N-bromosuccinimide (NBS) gives only one bromide (CXXV) (133). Similarly, oxidation of CXXVI with selenium



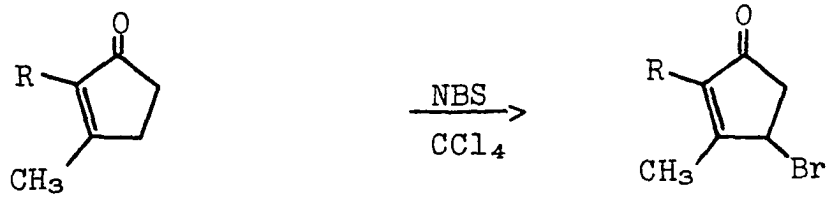
CXXIa CXXV

dioxide (134) gives the quinone CXXVII, which must mean that the first site of oxidation was at C-4.

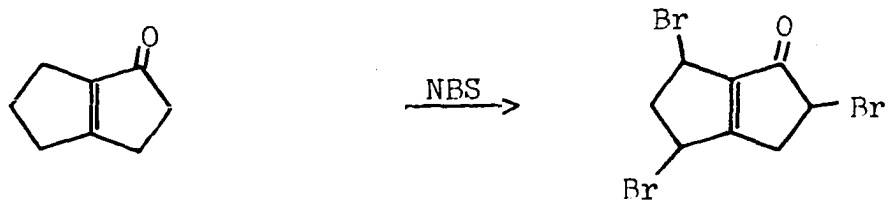


CXXVI CXXVII

Crombie, Elliott and Harper (135) have shown that the only mono-bromides formed in the reaction of NBS with 2-alkyl-3-methyl-2-cyclopentenones are the 4-bromo-derivatives. N-bromocussinimide reacts with bicyclo[3.3.0]oct-1(5)-en-2-one (CXXX) to give the tribromo-derivative CXXXI (136). We are not aware of analogous studies of ketones CXXIIa-CXXIVa.



CXXVIII CXXIX



CXXX CXXXI

BIBLIOGRAPHY

1. R. Dehl and G. K. Fraenkel, J. Chem. Phys., 39, 1793 (1963).

2. G. A. Russell and E. T. Strom, J. Amer. Chem. Soc., 86, 744 (1964).

3. G. A. Russell and E. R. Talaty, J. Amer. Chem. Soc., 86, 5345 (1964).

4. E. R. Talaty and G. A. Russell, J. Amer. Chem. Soc., 87, 4867 (1965).

5. E. R. Talaty and G. A. Russell, J. Org. Chem., 31, 3455 (1966).

6. G. A. Russell, E. R. Talaty, and R. H. Horrocks, J. Org. Chem., 32, 353 (1967).

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

8. G. A. Russell, E. T. Strom, E. R. Talaty, K.-Y. Chang, R. D. Stephens, and M. C. Young, Rec. Chem. Progr., 27, 3 (1966).

9. G. A. Russell, Science, 161, 423 (1968).

10. G. A. Russell in "Radical Ions", E. T. Kaiser and L. Kevan, ed., John Wiley and Sons, Inc., New York, N.Y., 1968, Chapter 3.

11. G. A. Russell, G. Holland, K.-Y. Chang, and L. H. Zalkow, Tetrahedron Lett., 1955 (1967).

12. G. A. Russell, G. W. Holland, and K.-Y. Chang, J. Amer. Chem. Soc., 89, 6629 (1967).

13. C. Heller and H. M. McConnell, J. Chem. Phys. 32, 1535 (1960).

14. S. Sternhell, Rev. Pure and Appl. Chem., 14, 15 (1964).

15. P. G. Gassman and R. L. Cryberg, J. Amer. Chem. Soc., 90, 1355 (1968).

16. L. Bouveault and G. H. Blanc, Bull. Soc. Chim. Fr., 29, 787 (1903); ibid., 31, 666, 672 (1904); ibid., Compt. rend., 136, 1676 (1903).

17. S. M. McElvain, Org. Reactions, 4, 256 (1948).

18. K. T. Finley, Chem. Rev., 64, 573 (1964).

19. E. van Heyningen, J. Amer. Chem. Soc., 74, 4861 (1952); ibid., 77, 4016 (1955).

20. J. M. Snell and S. M. McElvain, J. Amer. Chem. Soc., 53, 750 (1931).

21. K. T. Finley and N. A. Sasaki, J. Amer. Chem. Soc., 88, 4267 (1966).

22. A. C. Cope and E. C. Herrick, J. Amer. Chem. Soc., 72, 983 (1950).

23. U. Schräpler and K. Rühlmann, Chem. Ber., 97, 1383 (1964).

24. K. Rühlmann, H. Seefluth, and H. Becker, Chem. Ber., 100, 3820 (1967).

25. G. E. Gream and S. Worthley, Tetrahedron Lett., 3319 (1968).

26. J. J. Bloomfield, Tetrahedron Lett., 587 (1968).

27. J. J. Bloomfield, Tetrahedron Lett., 591 (1968).

28. G. A. Russell and G. R. Underwood, J. Phys. Chem., 72, 1074 (1968).

29. G. A. Russell and P. R. Whittle, J. Amer. Chem. Soc., 89, 6781 (1967).

30. Y. Deguchi, Bull. Chem. Soc. Jap., 35, 260 (1962).

31. K. Mukai, H. Nishiguchi, K. Ishizu, Y. Deguchi, and T. Takaki, Bull. Chem. Soc., Jap., 40, 2731 (1967).

32. K.-Y. Chang. Radical anions derived from bridged bicyclic α-diketones. Unpublished Ph.D. thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1965.

33. Y. Ōishi, K. Mukai, H. Nishiguchi, Y. Deguchi, and H. Takaki, Tetrahedron Lett., 4773 (1968).

34. J. Gendell, J. H. Freed, and G. K. Fraenkel, J. Chem. Phys., 37, 2832 (1962).

35. J. Oakes and M. C. R. Symons, Trans. Faraday Soc., 64, 2579 (1968).

36. F. J. Smentowski and G. R. Stevenson, J. Amer. Chem. Soc., 89, 5120 (1967).

37. G. A. Russell, P. R. Whittle, and J. McDonnell, J. Amer. Chem. Soc., 89, 5515 (1967).

38. J. J. McDonnell. Semidiones in the bicyclo[3.1.0]hexane system. Unpublished Ph.D. thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1968.

39. G. R. Underwood and R. S. Givens, J. Amer. Chem. Soc., 90, 3713 (1968).

40. G. A. Russell, J. McDonnell, and P. R. Whittle, J. Amer. Chem. Soc., 89, 5516 (1967).

41. R. E. Ireland and J. A. Marshall, J. Org. Chem., 27, 1615, 1620 (1962).

42. G. A. Russell and J. J. McDonnell, Tetrahedron Lett., 4213 (1968).

43. S. P. Acharya, Tetrahedron Lett., 4117 (1966).

44. S. P. Acharya and H. C. Brown, J. Amer. Chem. Soc., 89, 1925 (1967).

45. J. A. Marshall and W. I. Fanta, J. Org. Chem., 29, 2501 (1964).

46. W. G. Dauben and G. H. Berezin, J. Amer. Chem. Soc., 85, 468 (1963).

47. O. L. Chapman, H. G. Smith, and P. A. Barks, J. Amer. Chem. Soc., 85, 3171 (1963).

48. W. G. Dauben and D. A. Cox, J. Amer. Chem. Soc., 85, 2130 (1963).

49. D. Kosman and L. M. Stock, J. Amer. Chem. Soc., 88, 843 (1966).

50a. S. F. Nelsen and E. D. Seppanen, J. Amer. Chem. Soc., 89, 5740 (1967).

50b. S. F. Nelsen and B. M. Trost, Tetrahedron Lett., 5737 (1966).

51. D. Kosman and L. M. Stock, Chem. Commun., 551 (1968).

52. E. L. Cochran, F. J. Adrian, and V. A. Bowers, J. Chem. Phys., 40, 213 (1964).

53. K. E. Anderson, D. Kosman, C. J. Mayers, B. P. Ruekberg, and L. M. Stock, J. Amer. Chem. Soc., 90, 7168 (1968).

54. D. Kosman and L. M. Stock, Tetrahedron Lett., 1511 (1967).

55. J. C. Stowell, J. Org. Chem., 32, 2360 (1967).

56. F. Dallacker, I. Alroggen, H. Krings, B. Laurs, and M. Lipp, Ann. Chem., 647, 23 (1961).

57. A. H. Beckett, R. G. Lingard, and B. A. Mulley, J. Chem. Soc., 3328 (1953).

58. A. H. Beckett and B. A. Mulley, J. Chem. Soc., 4159 (1955).

59. A. P. Terent'ev, L. I. Belen'kiĭ, and L. A. Yanovskaya, J. Gen. Chem. U.S.S.R., 24, 1251 (1954).

60. B. M. Mikhâilov, Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk, 420 (1948); Chem. Abstracts, 43, 208g (1949).

61. P. Brown and R. C. Cookson, Tetrahedron, 21, 1993 (1965).

62. N. Buu-Hoï and N. Hoan, J. Org. Chem., 16, 874 (1951).

63. R. O. C. Norman and W. A. Waters, J. Chem. Soc., 167 (1958).

64. A. H. Beckett and R. G. Lingard, J. Chem. Soc., 588 (1961).

65. O. Wallach, Chem. Ber., 28, 31 (1895).

66. F. W. Semmler, Chem. Ber., 36, 4367 (1903); ibid., 40, 5017 (1907).

67. R. H. Eastman and J. C. Selover, J. Amer. Chem. Soc., 76, 4118 (1954).

68. W. I. Fanta and W. F. Erman, J. Org. Chem., 33, 1656 (1968).

69. O. Wallach, Ann. Chem., 359, 265 (1908).

70. R. M. Acheson and R. Robinson, J. Chem. Soc., 1127 (1952).

71. E. LeGoff, J. Org. Chem., 29, 2048 (1964).

72. D. H. Marr and J. B. Stothers, Can. J. Chem., 45, 225 (1967).

73. J. Meinwald, S. S. Labana, and M. S. Chadha, J. Amer. Chem. Soc., 85, 582 (1963).

74. M. Rey and A. S. Dreiding, Helv. Chim. Acta, 48, 1985 (1965).

75. J. R. Holum, J. Org. Chem., 26, 4814 (1961).

76. D. W. Mathieson, J. Chem. Soc., 3248 (1953).

77. S. Dev, J. Indian Chem. Soc., 34, 169 (1957).

78. J. R. Williams and H. Ziffer, Chem. Commun., 194 (1967).

79. E. L. Eliel and C. A. Lukach, J. Amer. Chem. Soc., 79, 5986 (1957).

80. E. D. Bergmann and R. Corett, J. Org. Chem., 23, 1507 (1958).

81. J. L. Simonsen, J. Chem. Soc., 121, 2292 (1922).

82. K. Piatkowski, H. Kuczynski, and A. Kubik, Rocz. Chem., 40, 213 (1966).

83. E. J. Corey and M. Chaykovsky, J. Amer. Chem. Soc., 87, 1353 (1965).

84. O. L. Chapman, H. G. Smith, and R. W. King, J. Amer. Chem. Soc., 85, 803 (1963).

85. E. J. Forbes, J. Chem. Soc., 3864 (1955).

86. R. Criegee and H. Furrer, Chem. Ber., 97, 2949 (1964).

87. P. E. Eaton, Tetrahedron Lett., 3695 (1964).

88. R. L. Cargill, J. R. Damewood, and M. M. Cooper, J. Amer. Chem. Soc., 88, 1330 (1966).

89. R. L. Cargill, M. E. Beckham. A. E. Siebert, and J. Dorn, J. Org. Chem., 30, 3647 (1965).

90. N. L. Allinger and L. A. Tushaus, J. Org. Chem., 30, 1945 (1965).

91. J. Meinwald and B. E. Kaplan, J. Amer. Chem. Soc., 89, 2611 (1967).

92. W. H. Perkin, Jr., and J. L. Simonsen, J. Chem. Soc., 95, 1166 (1909).

93. R. T. LaLonde and R. I. Aksentijevich, Tetrahedron Lett., 23 (1965).

94. F. Lautenschlaeger and G. F. Wright, Can. J. Chem., 41, 863 (1963).

95. W. von E. Doering, L. H. Knox, and M. Jones, Jr., J. Org. Chem., 24, 136 (1959).

96. D. D. K. Chiu and G. F. Wright, Can. J. Chem., 37, 1425 (1959).

97. T. F. West, J. Chem. Soc., 140 (1941).

98. W. Reppe, O. Schlichting, K. Klager, and T. Toepel, Ann. Chem., 560, 1 (1948).

99. W. G. Dauben and D. L. Whalen, Tetrahedron Lett., 3743 (1966).

100. W. E. Bachmann and L. B. Scott, J. Amer. Chem. Soc., 70, 1458 (1948).

101. W. E. Bachmann and M. C. Kloetzel, J. Amer. Chem. Soc., 60, 481 (1938).

102. L. J. Andrews and R. M. Keefer, J. Amer. Chem. Soc., 77, 6284 (1955).

103. G. A. Russell and S. A. Weiner, J. Org. Chem., 31, 248 (1966).

104. J. Sauer, H. Wiest, and A. Mielert, Chem. Ber., 97, 3183 (1964).

105. K. Ziegler, W. Flaig, and G. Velling, Ann. Chem., 567, 204 (1950).

106. S. B. Soloway, J. Amer. Chem. Soc., 74, 1027 (1952).

107. H. Bode, Chem. Ber., 70, 1167 (1937).

108. C. F. Huebner, E. Donoghue, L. Dorfman, F. A. Stuber, N. Danieli, and E. Wenkert, Tetrahedron Lett., 1185 (1966).

109. G. N. Schrauzer and P. Glockner, Chem. Ber., 97, 2451 (1964).

110. K. Alder and R. Rühmann, Ann. Chem., 566, 1 (1950).

111. E. P. Kohler, M. Tishler, H. Potter, and H. T. Thompson, J. Amer. Chem. Soc., 61, 1057 (1939).

112. L. L. McCoy, J. Amer. Chem. Soc., 80, 6568 (1958).

113. E. R. Buchman, A. O. Reims, T. Skei, and M. J. Schlatter, J. Amer. Chem. Soc., 64, 2696 (1942).

114. H. A. Smith and T. Fort, Jr., J. Amer. Chem. Soc., 78, 4000 (1956).

115. K. Alder and H. A. Dortmann, Chem. Ber., 87, 1492 (1954).

116. E. H. Farmer and F. L. Warren, J. Chem. Soc., 897 (1929).

117. I. N. Nazarov and V. F. Kucherov, Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk, 289 (1952); Chem. Abstracts, 47, 5363 (1953).

118. E. Vogel, Ann. Chem., 615, 1 (1958).

119. S. G. Cohen, R. Zand, and C. Steel, J. Amer. Chem. Soc., 83, 2895 (1961).

120. R. B. Woodward and H. Baer, J. Amer. Chem. Soc., 70, 1161 (1948).

121. J. Jolivet, Ann. Chim. (Paris), 5, 1165 (1960).

122. G. O. Schenck, W. Hartmann, and R. Steinmetz, Chem. Ber., 96, 498 (1963).

123. P. R. Story, J. Amer. Chem. Soc., 83, 3347 (1961).

124. H. C. Brown and H. M. Bell, J. Amer. Chem. Soc., 85, 2324 (1963).

125. J. T. Lumb and G. H. Whitham, Tetrahedron, 21, 499 (1965).

126. C. A. Grob and J. Hostynek, Helv. Chem. Acta, 46, 1676 (1963).

127. W. Treibs and H. Albrecht, J. Prakt. Chem., 8, (Series 4), 123 (1959).

128. R. Huisgen, W. Scheer, G. Szeimies, and H. Huber, Tetrahedron Lett., 397 (1966).

129. G. A. Russell, E. G. Janzen, and E. T. Strom, J. Amer. Chem. Soc., 86, 1807 (1964).

130. G. A. Russell, E. T. Strom, E. R. Talaty, and S. A. Weiner, J. Amer. Chem. Soc., 88, 1998 (1966).

131. J. J. Bloomfield, R. G. Todd, and L. T. Takahashi, J. Org. Chem., 28, 1474 (1963).

132. H. L. Malkus. Conformational studies of acyclic semidiones. Unpublished Ph.D. thesis. Ames, Iowa, Library. Iowa State University of Science and Technology. 1968.

133. A. J. B. Edgar, S. H. Harper, and M. A. Kazi, J. Chem. Soc., 1083 (1957).

134. E. Dane and J. Schmitt, Ann. Chem., 536, 196 (1938).

135. L. Crombie, M. Elliott, and S. H. Harper, J. Chem. Soc., 971 (1950).

136. E. Ghera, R. Szpigielman, and E. Wenkert, J. Chem. Soc., C, 1479 (1966).

ACKNOWLEDGEMENTS

I would like to especially thank Dr. Glen A. Russell for his patience and understanding throughout his direction of this research. I consider myself very fortunate to have been a member of his research group.

My thanks go to the various members of the Russell group for many helpful discussions and for just being themselves. Thanks also to the storeroom attendants and technicians who have helped make my research efforts a pleasure.

I am most grateful to my wife, Donna, whose love and understanding has made my work so much more meaningful. Her help with the preparation of the figures in this thesis is greatly appreciated. Although our son, Bruce, hardly realizes it now, his timely birth (March 24, 1969) played quite a role in the completion of this thesis.

My parents deserve a special vote of thanks for their unselfish encouragement and support. Thanks also to my wife's parents, who have been more than gracious to me in the time I have known them.

Finally, I would like to thank the National Aeronautics and Space Administration and the Petroleum Research Foundation for financial support in the form of fellowships during the course of this work.