

1974

Studies in valence isomerism of unsaturated paramagnetic species

Edward Joseph Goettert
Iowa State University

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STUDIES IN VALENCE ISOMERISM OF
UNSATURATED PARAMAGNETIC SPECIES.

Iowa State University, Ph.D., 1974
Chemistry, organic

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Studies in valence isomerism of
unsaturated paramagnetic species

by

Edward Joseph Goettert

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

Department: Chemistry
Major: Organic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

For the Major ~~Department~~

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For the Graduate College

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Ames, Iowa

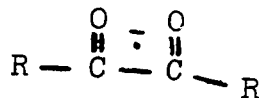
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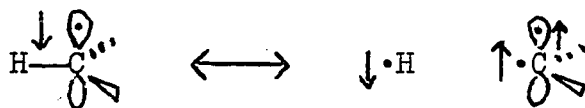
INTRODUCTION

The semidione radical anion, which is the one electron reduction product of a diketone, has been the subject of much



work and has been well reviewed (1,2,3). Electron spin resonance studies utilizing the semidione as a spin label have been undertaken in the areas of structural and conformation analysis as well as in the investigation of the mechanism of spin propagation.

Basically, there are two general modes of interaction between the unpaired electron and the nuclei in the molecule containing this electron, spin polarization and hyperconjugation. An example of spin polarization can be found in the interaction between an electron in a p-orbital of an sp^2 carbon with an attached hydrogen atom. The sigma bond is



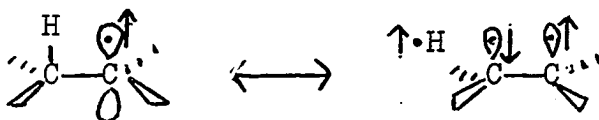
polarized placing spin density on the hydrogen opposite in sign to the spin of the radical as a unit. The extent of this interaction can be determined by McConnell's equation

$$a^{\text{H}} = Q p_c$$

(4), where Q is a constant whose value and sign depend on the

type of radical and the hybridization of the radical center and p is the spin density at the radical center.

Hyperconjugation is an important spin interaction mechanism for atoms two bonds away from the radical center.

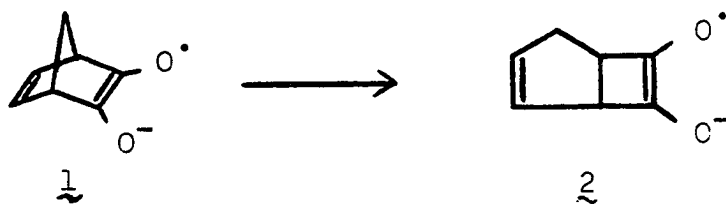


This interaction is maximized when the carbon-hydrogen bond and the orbital are contained in the same plane as (5)

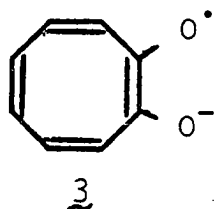
$$a^{\text{H}} = \beta p_c \cos^2 \theta$$

where β is a constant dependent on the charge of the radical, usually taken as 40 for anion radicals, and θ is the dihedral angle between the C-H bond and the p orbital. When inversion or rotation of the interacting group takes place so that the dihedral angle is not constant under experimental conditions, an averaging value for $\cos^2 \theta$ must be used, for example, 0.5 for a freely rotating methyl group.

Since the magnitude of the hyperfine splitting constants and the number and type of hydrogens observed in an electron spin resonance spectrum are dependent upon the geometry and symmetry incorporated in the molecule under investigation, it should be possible to observe any rearrangement that takes place in the radical. Indeed, Schmitt (6) claims to observe the rearrangement of bicyclo[2.2.1]hept-5-en-2,3-semidione 1 to bicyclo[3.2.0]hept-2-en-6,7-semidione 2.

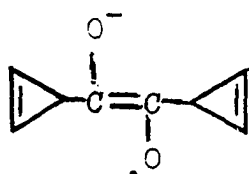
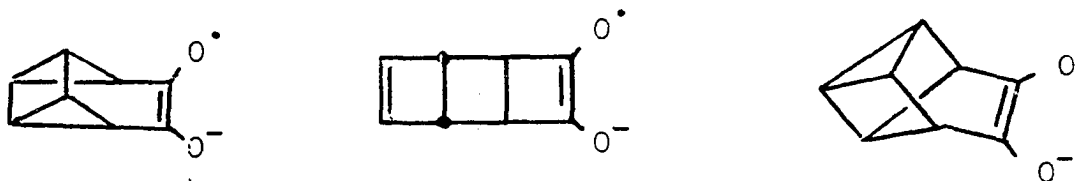
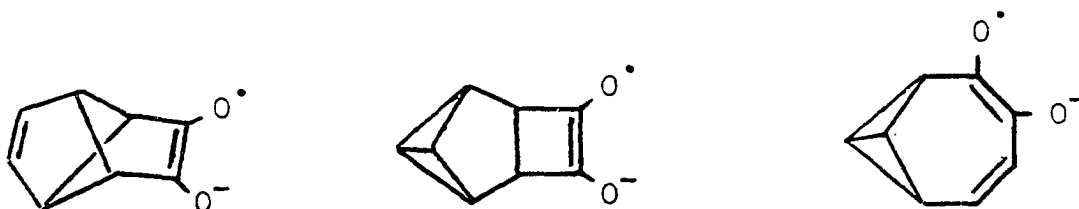
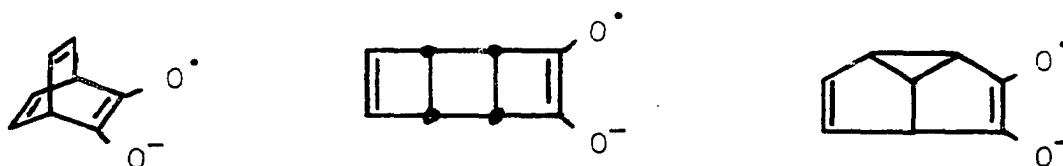
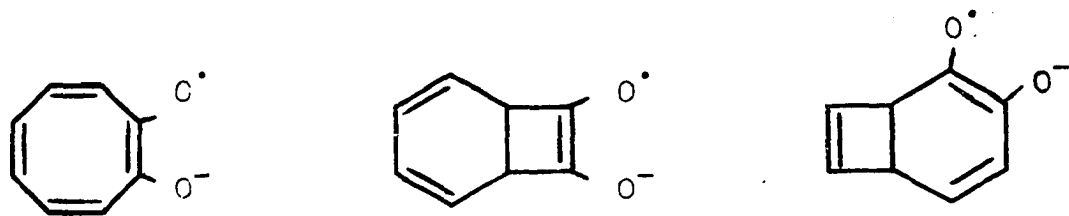


It was the primary purpose of this work to synthesize cyclooctatriene semidione 3, in order to gain an insight into



its geometry and to observe any possible rearrangements that may occur. The number of valence isomers of cyclooctatriene semidione (Table 1) is great, and the possible rearrangements are legion. A secondary goal of this work was the synthesis of other cyclic eight membered semidiones with a lesser degree of unsaturation.

Table 1. Some valence isomers of cyclooctatriene semidiones



cis and trans

HISTORICAL

Cyclooctatetraene

The chemistry and structure of cyclooctatetraene and its derivatives have been the subject of considerable study (7, 8,9). Cyclooctatetraene was first prepared by Willstätter and co-workers in a thirteen step low yield degradative procedure from pseudopelletierine 4, an alkaloid obtained



4

from pomegranates (10,11). However, it was not until Reppe's development in 1948 of a catalytic procedure for the synthesis of cyclooctatetraene from acetylene in tetrahydrofuran solution in the presence of nickel cyanide that it became readily available (12).

Cyclooctatetraene is a yellow liquid, olefinic in nature, with little or no aromatic character. The C=C stretching frequency in the infrared is observed at 1639 cm^{-1} which is a typical value for a nonconjugated aliphatic carbon-carbon double bond (13). The ultraviolet spectrum of cyclooctatetraene does not exhibit the sharp fine structure shown by benzene but rather two broad indefinite inflections (14). Also, the nuclear magnetic resonance spectrum consists of a

single resonance at 5.5 δ , clearly in the olefinic region (15). Indeed, the electron diffraction studies indicate a tub-like structure with the following dimensions: C-C, 1.46-1.50 \AA ; C=C, 1.33-1.35 \AA ; C-H, 1.09-1.13 \AA ; C=C-C angle 124-126 $^\circ$; and C=C-H angle 118 $^\circ$ (compared to the usual

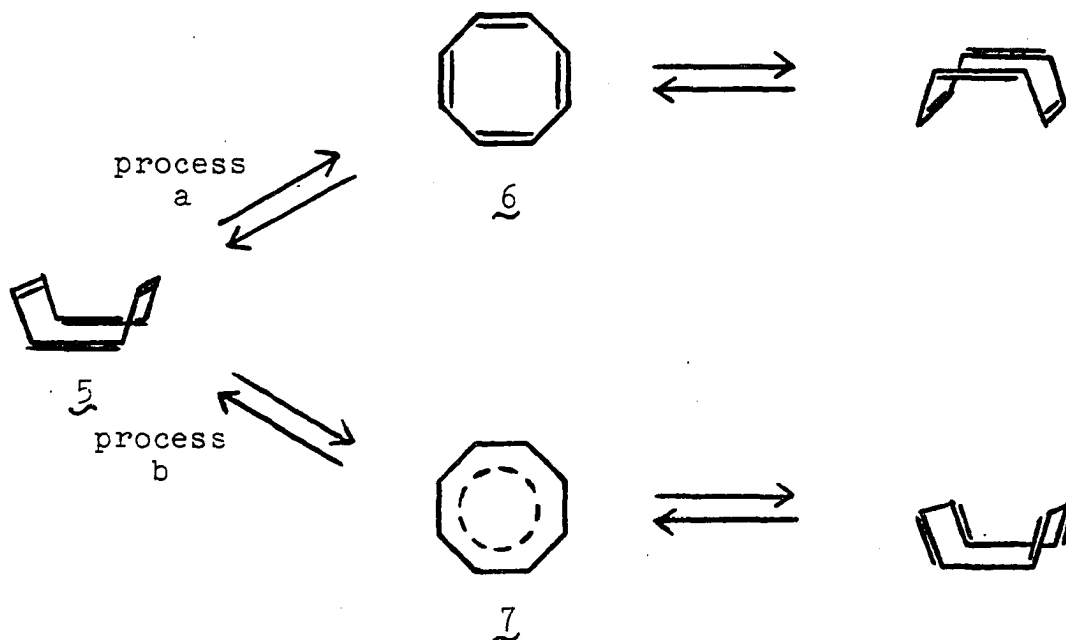


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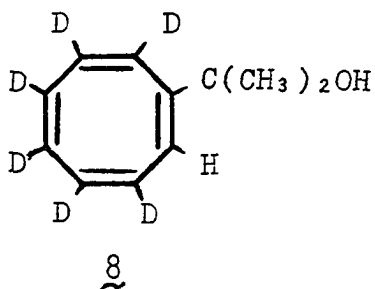
aliphatic interatomic dimensions of 1.54 \AA ; 1.34 \AA ; 1.13 \AA ; 120 $^\circ$; and 120 $^\circ$, respectively) (16,17). Clearly, the double bonds of cyclooctatetraene are isolated in that π overlap between the double bonds is sterically inhibited. This fact is borne out by the low value of the resonance energy (2.4-4.8 kcal/mole) as determined by its heat of combustion and heat of hydrogenation (18).

Since the nuclear magnetic spectrum of cyclooctatetraene is a singlet at room temperature, a process must exist that imparts magnetic equivalence to all protons. Indeed, it is possible to observe magnetic nonequivalence by low temperature nmr spectroscopy (19,20,21). Two possible time averaging processes are ring inversion (process a) and bond migration (process b). Presumably, both processes proceed via planar transition states, process a via a planar molecule with alternating single and

double bonds 6 and process b via a symmetrical planar state 7. The two processes can be distinguished for the substituted

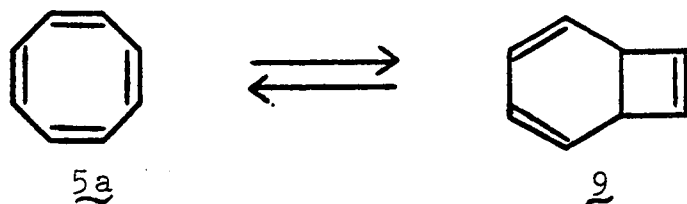


cyclooctatetraene 8. At -2° , the ring inversion requires an

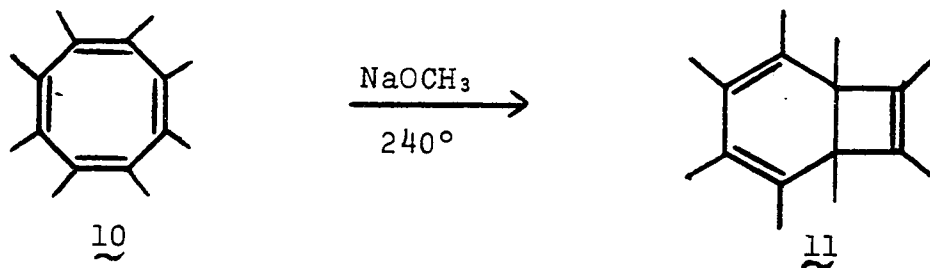


activation energy of 14.7 kcal/mole whereas the bond shift requires 17.1 kcal/mole. Thus it can be seen that for 8, the planar symmetrical transition state 7 is more energetic than the planar alternating bond structure 6 by 2.4 kcal/mole (21).

Cyclooctatetraene also exists in equilibrium with its bicyclic isomer (22,23,24), and the concentration of the



bicyclic form has been measured as 0.01% at 100° (25). In fact, the rate determining step for Diels-Alder cycloadditions to cyclooctatetraene consists of the bicyclic isomer formation (25). Low temperature photolysis of cyclooctatetraene results in the formation of 9 (26,27), which however reverts back to the monocyclic form at 0° (28). Most cyclooctatetraene derivatives are most stable in the monocyclic form; however, an exception is octamethylcyclooctatetraene 10, which is irreversibly converted to octamethylbicyclo[4.2.0]octa-2,4,7-triene 11 upon extensive heating with base (29).

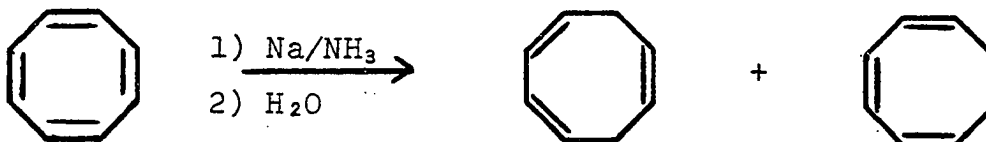


Also, many other interconversions in the C_8H_8 system occur involving cyclooctatetraene upon pyrolysis or photolysis of which the following are typical.

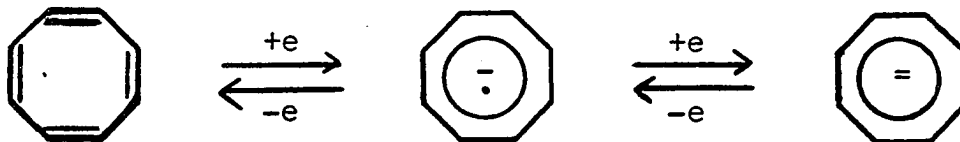


Cyclooctatetraene Anions

Treatment of cyclooctatetraene with alkali metals results in the facile reduction of the molecule (12). The ions formed react with water to give a mixture of 1,3,5 and 1,3,6 cyclooctatrienes (34) and with carbon dioxide to

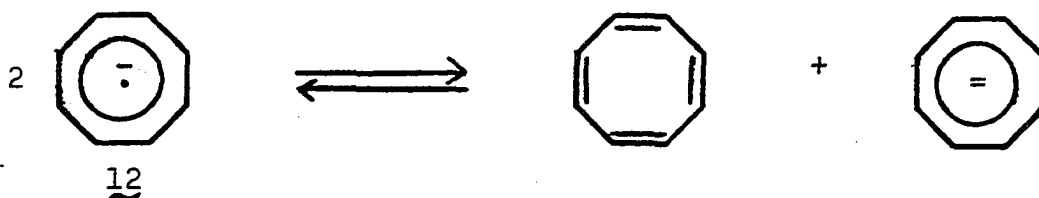


give a dicarboxylic acid (12). Polarographic studies show that cyclooctatetraene is reduced at the high wave potential of -1.5 volts (35) and that the reduction involved a two electron process independent of pH (36,37) indicating that protons are not involved in the reduction step. When the reduction by potassium in tetrahydrofuran is studied by nmr spectroscopy, the signal due to cyclooctatetraene is seen to decrease accompanied by the appearance of a broad band. The broad band sharpens into a singlet, δ 5.7, after two equivalents of potassium have been consumed (38,39). The



infrared spectrum is simple with bands at 2994, 1431, 880, and 684 cm^{-1} (40,41), and the ultraviolet spectrum is consistent with a planar structure having all bond lengths equal (42).

The cyclooctatetraene radical anion 12 has also been observed and exists in equilibrium with the neutral compound and the dianion (43,44). The electron spin resonance line

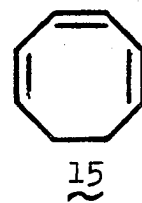
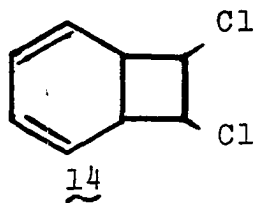
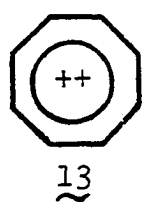


width studies indicate the occurrence of rapid electron exchange between the radical anion and the dianion, suggesting that the two ions have similar geometries. Indeed, the esr hyperfine structure of 12 shows eight equivalent hydrogens with a splitting of 3.21 gauss (45) supporting a planar structure. In fact, in the reduction of cyclooctatetraene to the dianion, the rate determining step is the addition of the first electron probably due to the barrier which had to be overcome to flatten the ring. Once the molecule is planar, addition of another electron to the dianion occurs more readily (46).

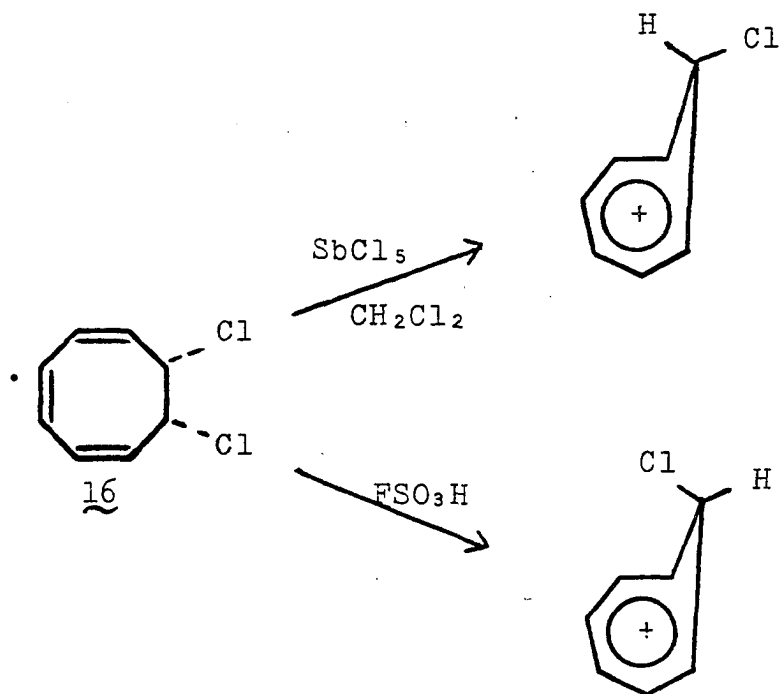
Cyclooctatetraene Cations

The cations of cyclooctatetraene have proved to be much more elusive than the anions. The electrochemical oxidation of cyclooctatetraene in acetic acid buffered with acetate ion gives a complex mixture of acetates (47,48). The reaction may proceed through the dication 13, but this is doubtful.

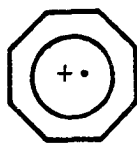
Also, attempts to generate the dication 13 by treatment of 7,8-dichlorobicyclo[4.2.0]octa-2,4-diene 14 with stannic



chloride or 1,3,5-cyclooctatriene 15 with hydride abstractors proved unsuccessful (49). Indeed, when cis-7,8-dichlorocycloocta-1,3,5-triene 16 is treated with antimony pentachloride or with fluorosulfonic acid, 8-chlorohomotropylium cations are formed (50,51).



The electron spin resonance spectrum of cyclooctatetraene radical cation 17 was obtained in a rapid mixing



17

flow system utilizing cobaltic ion as an oxidant in trifluoroacetic acid (52). The spectrum consisted of seven equally spaced lines ($a^H = 1.5$ G); presumably the splitting was caused by eight equivalent hydrogens with the two outer lines being too small to be detected. By analogy to aromatic ions (53), the splitting for the radical cation should be larger than the corresponding radical anion; however, this relationship does not hold for cyclooctatetraene, 1.5 G for the cation compared to 3.2 G for the anion (45). A smaller splitting for the cation supports a nonplanar equilibrating configuration for the cation.

Dihalocyclooctatriene

The addition of a molecule of halogen to cyclooctatetraene has been well studied (54) and the dihalide is known to exist as trans-7,8-dihalobicyclo[4.2.0]cycloocta-2,4-diene at room temperature. This bicyclic diene appears to be a free spirit, rearranging, fragmenting, and substituting at will. A summary of its chemistry is given in Figure 1.

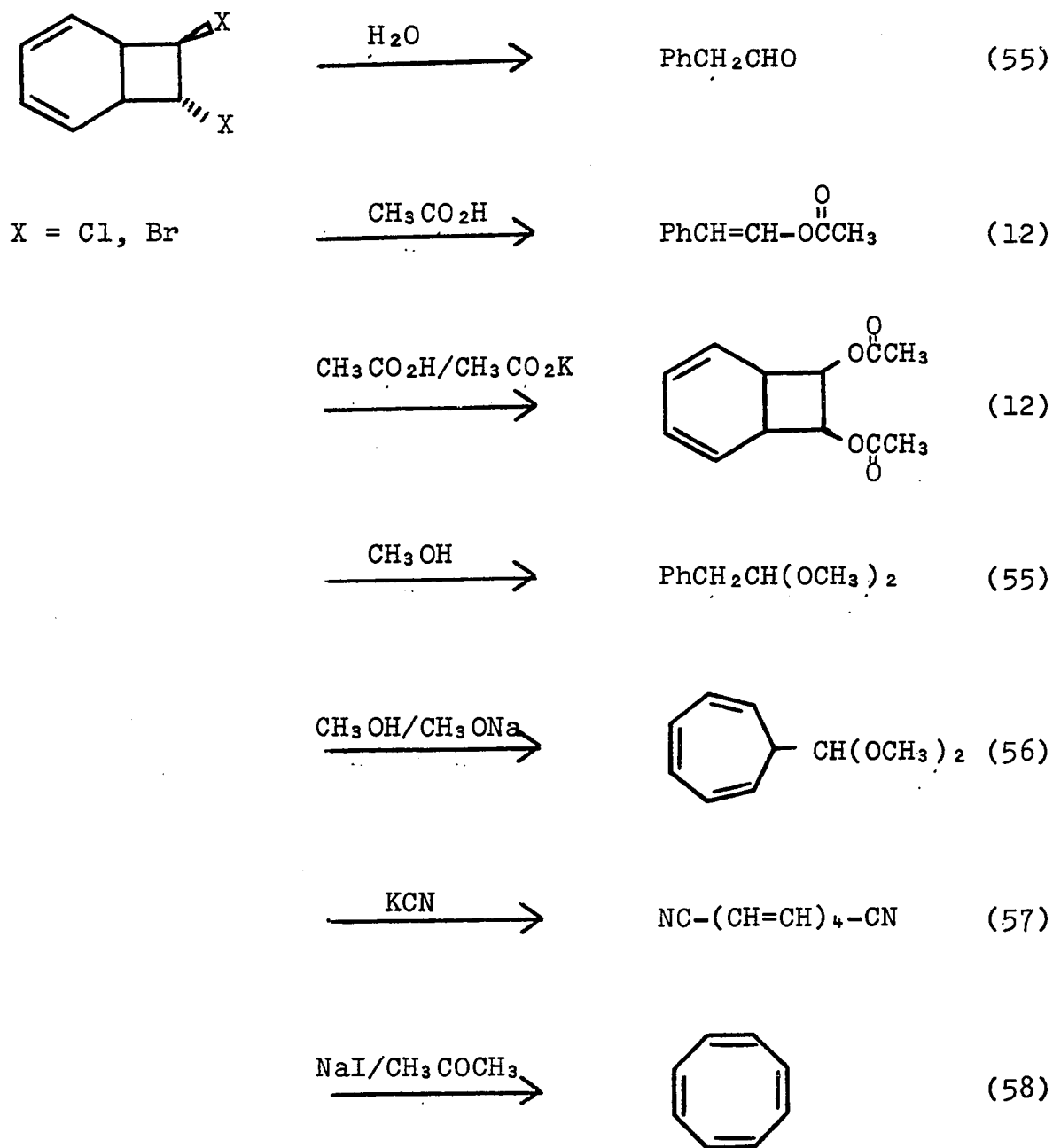
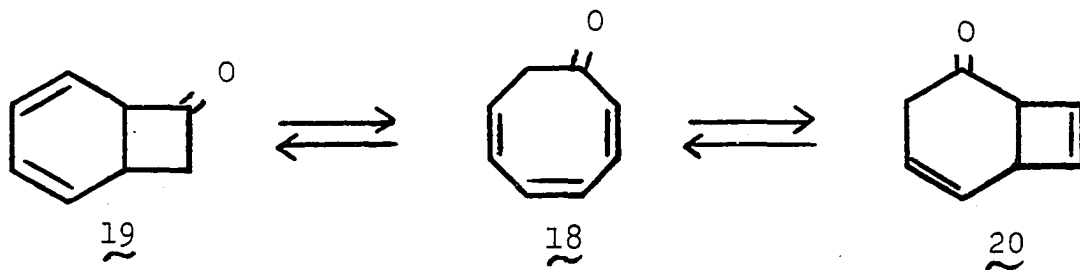


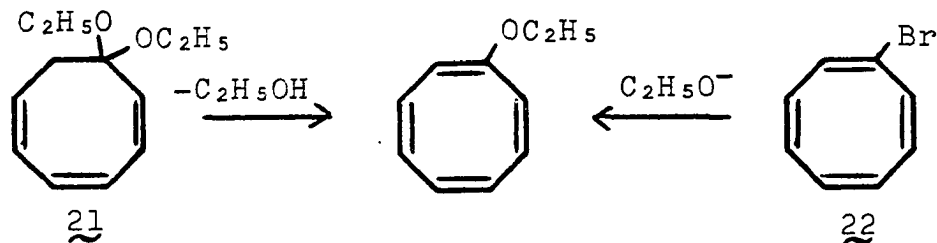
Figure 1. Reactions of trans-7,8-dihalobicyclo[4.2.0]cyclo-octa-2,4-diene at room temperature

2,4,6-Cyclooctatrien-1-one

Cyclooctatrienone 18 exists in equilibrium with its bicyclic valence tautomer 19, bicyclo[4.2.0]octa-2,4-dien-7-one, to the extent of 5% at room temperature (59-62).

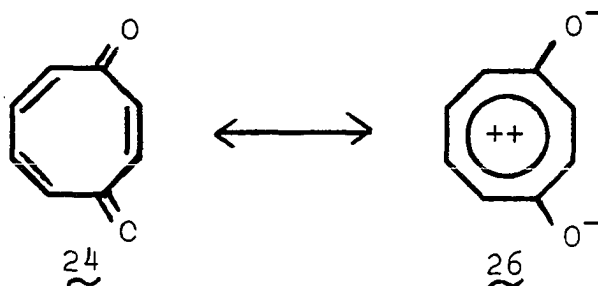
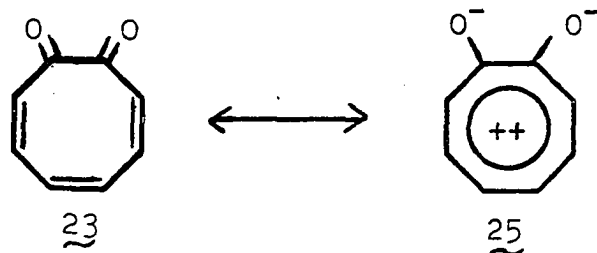


Irradiation of the monocyclic ketone 18 results in the formation of a second valence isomer 20, bicyclo[4.2.0]octa-4,7-dien-2-one, which reverts back to the monocyclic form upon standing in the dark at room temperature. The trienone 18 shows no tendency to enolize, and enolic derivatives are obtainable only by indirect means; ethoxycyclooctatetraene has been produced by acid or base catalyzed elimination of ethanol from the diethyl ketal 21 (61), by the substitution of ethoxide for bromide in 22 (63), but not directly from the ketone.

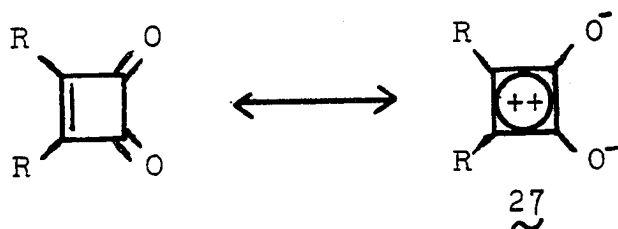


Cyclooctatrienediones

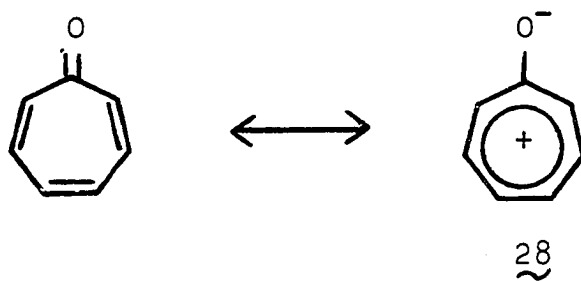
Cyclooctatrienediones, both the 1,2 isomer 23 and the 1,4 isomer 24, are of interest because of the possible aromatic character of the ring embodying the 6π electron cyclooctatetraene dication. However, the Coulombic



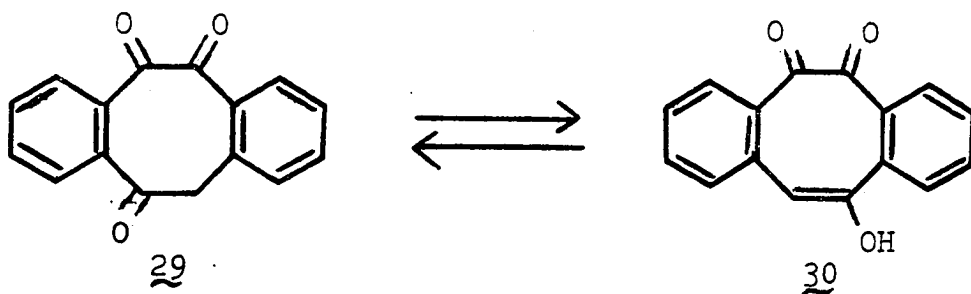
interaction between the negative charges on the oxygen atoms and the charge separation in the canonical forms 25 and 26 would tend to increase the energy of these structures and reduce their effectiveness in conferring aromaticity on the diones. The related cyclobutenediones do indeed show increased stability presumably due to resonance stabilization (64). However, the requirement of a planar configuration in 27 does not necessitate increased angle strain relative to



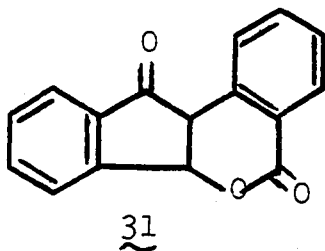
nonplanar configurations. In the more analogous case of the larger ring in tropone, there appears to be only a minor contribution from the zwitterionic form 28 (65-67).



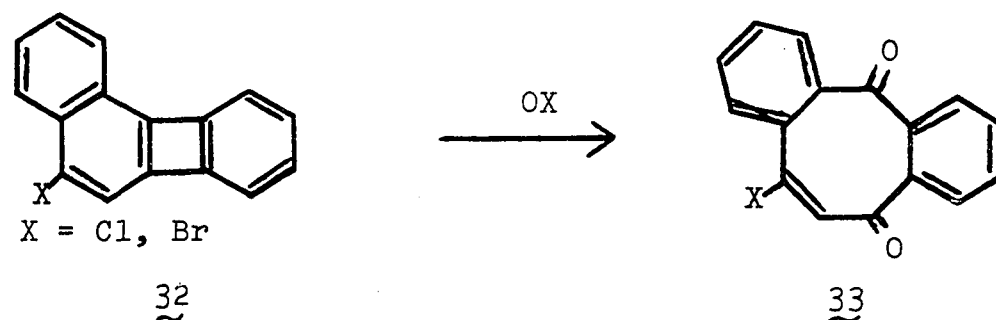
One of the first synthetic approaches to a cycloocta-trienedione derivative was aimed at preparation of the trione 29 which upon enolization would yield the required system 30



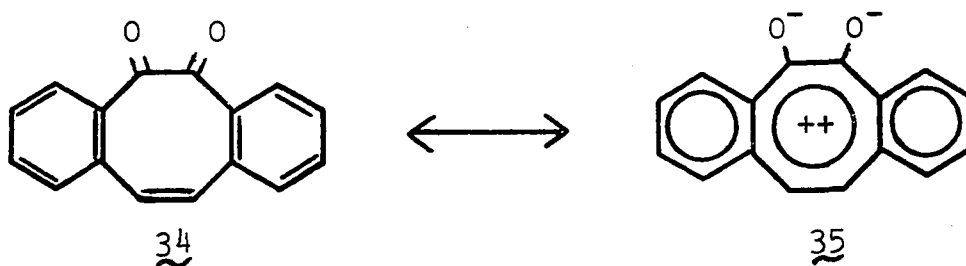
(68). However, the compound thought to be 29 was later found to possess a different structure, that of 31 (69,70).



Later attempts to obtain 29 also proved unsuccessful (71). Cava and Ratts (72), however, reported the formation of a halogen substituted derivative of the 1,4-dione 33 upon oxidation of the biphenylene 32.



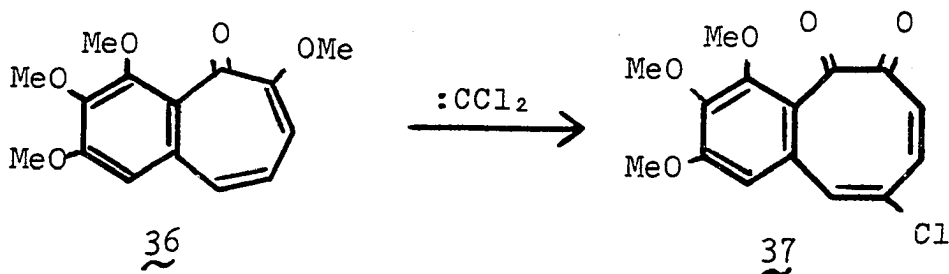
Yates and co-workers (73) were successful in preparing dibenzocyclooctatrienedione 34. However, the diketone was



found to be nonplanar and nonaromatic on the basis of ir, uv, and nmr spectral data, dipole moment data, and its electrolytic reduction potential with no contribution from

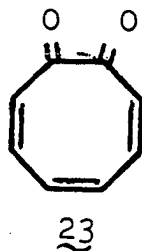
canonical form 35. The presence of the two benzene rings adjacent to the eight membered ring could lessen the aromaticity of this ring due to their tendency to incorporate the π electrons in their own aromatic systems (74), and, thus, the lack of aromaticity in 34 may not be a true indication of the state of the unsubstituted cyclooctatrienedione.

Attempts by McIntyre and co-workers (75) to synthesize the monobenzo derivative were unsuccessful. However, Tsunetsugu and co-workers (76) claimed to have made a substituted benzocyclooctatrienedione 37 in three percent yield by the addition of dichlorocarbene to a substituted tropone 36. On the basis of the ir ($C=O$, 1723 cm^{-1}) and



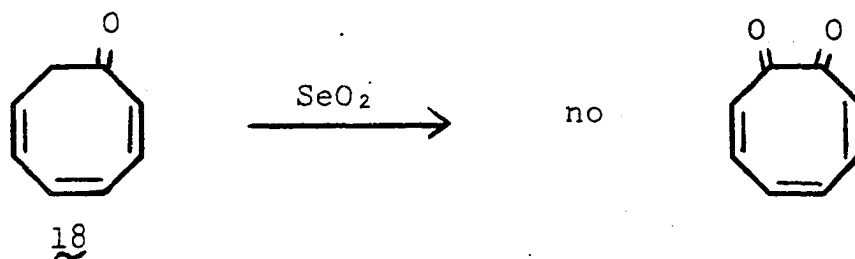
nmr (signals at δ 6.35 and δ 6.72) it was concluded that the eight membered ring was not planar.

The unsubstituted 1,2-cyclooctatrienedione 23, although

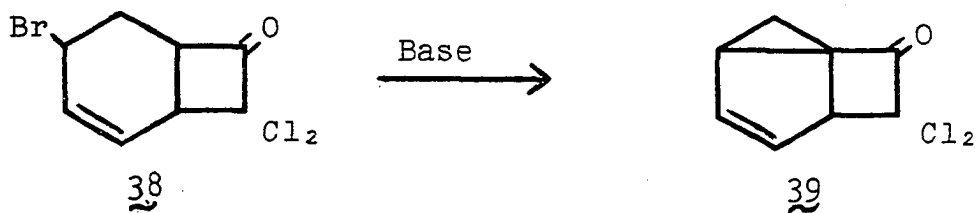


theoretically a possible aromatic compound, has never been

prepared despite much work toward its synthesis. Gund (77) attempted to obtain the dione directly through oxidation of the trienone 18 but obtained only starting material and

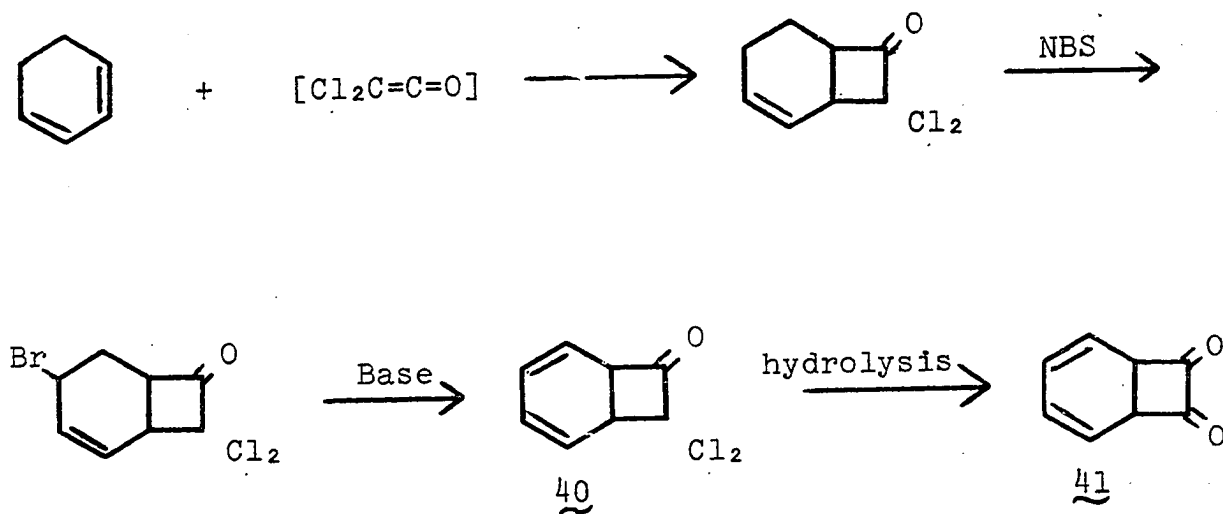


aromatics. An approach by Gund to the bicyclic isomer, bicyclo[4.2.0]octa-2,4-dien-7,8-dione 41, outlined in Scheme 1, proved unsuccessful when the dehydrohalogenation step resulted in production of a cyclopropyl derivative 39 rather than the anticipated diene 40. Isomerization of 39 to the diene could not be achieved.

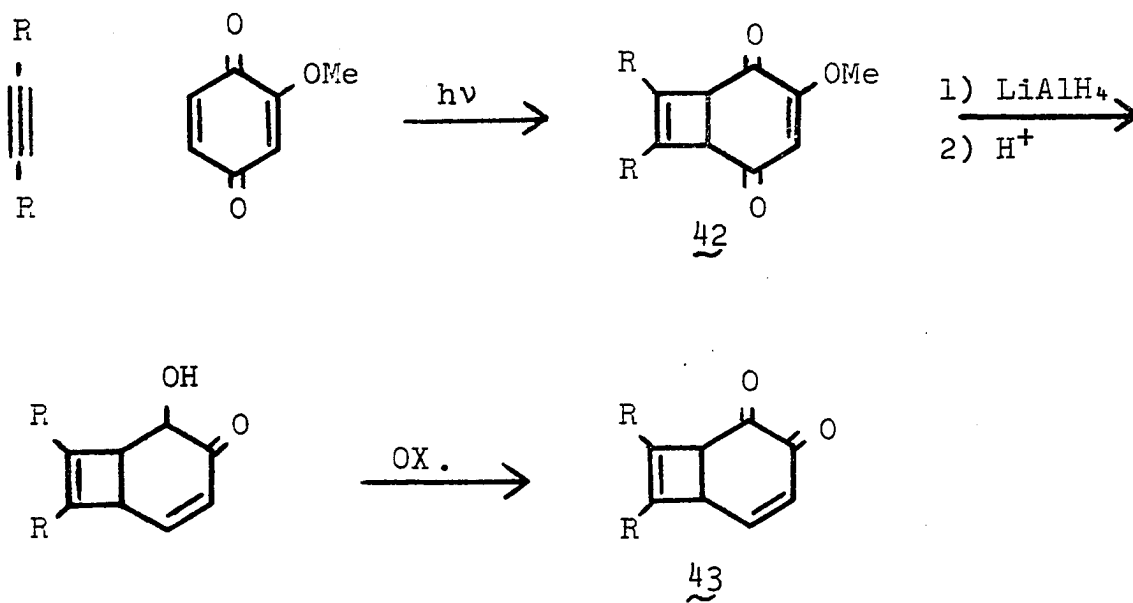


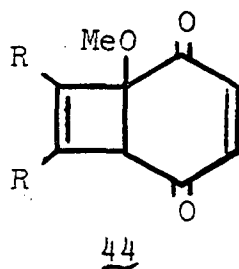
Pappas and co-workers (78) wished to prepare the other bicyclic isomer, bicyclo[4.2.0]octa-4,7-diene-2,3-dione through a photo addition sequence (Scheme 2). However, the desired photo adduct 42 was not obtained; instead, the acetylene added to the methoxy substituted double bond giving the methoxy substituent at the bridgehead 44.

Scheme 1

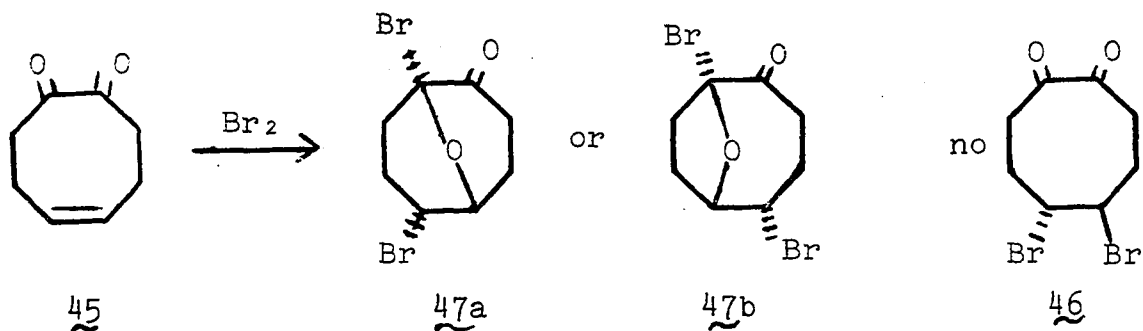


Scheme 2



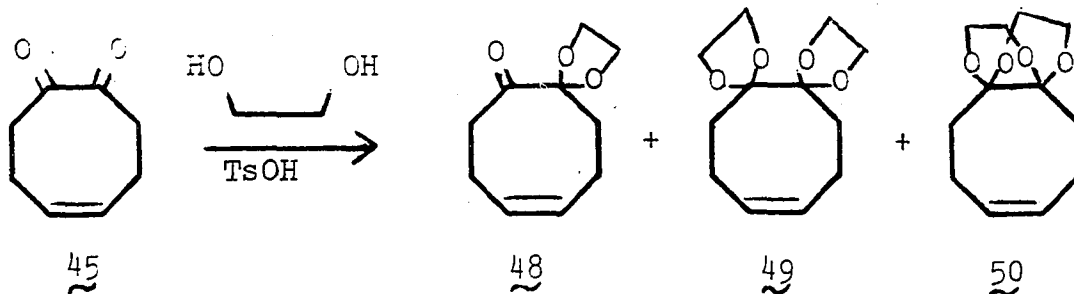


Yates and co-workers (79) approached the synthetic problem starting with *cis*-5-cyclooctene-1,2-dione 45. Bromination of 45 did not result in production of the expected *trans* bromide 46; instead, the reaction gave a

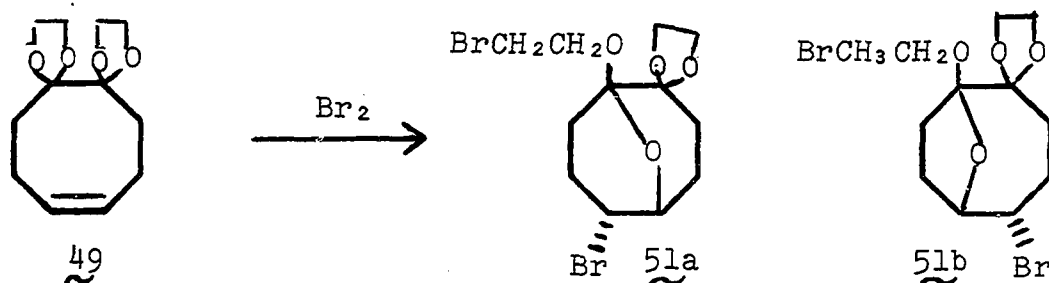


dibromide whose structure could be assigned as 47a or 47b. Attempted bromination of 45 with *N*-bromosuccinimide gave intractable tarry mixtures.

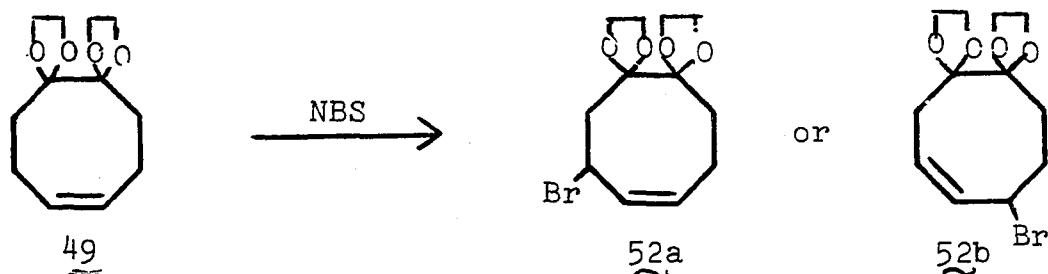
Treatment of 45 with ethylene glycol and *p*-toluenesulfonic acid in boiling dichloromethane gave a mixture of



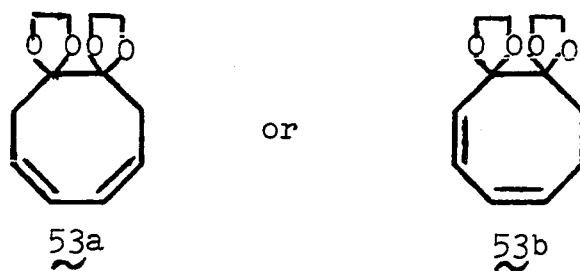
three ketals, 48, 49, and 50. Bromination of the diketal 49 with bromine or pyridinium perbromide again gave an unexpected dibromide containing a bromine atom in an exocyclic side chain, structure 51a or 51b. Bromination of 45 on a small



scale with N-bromosuccinimide or 1,3-dibromo-5,5-dimethylhydantoin gave a monobromocompound that can be formulated as 52a or 52b in quite low yields, but larger scale reactions

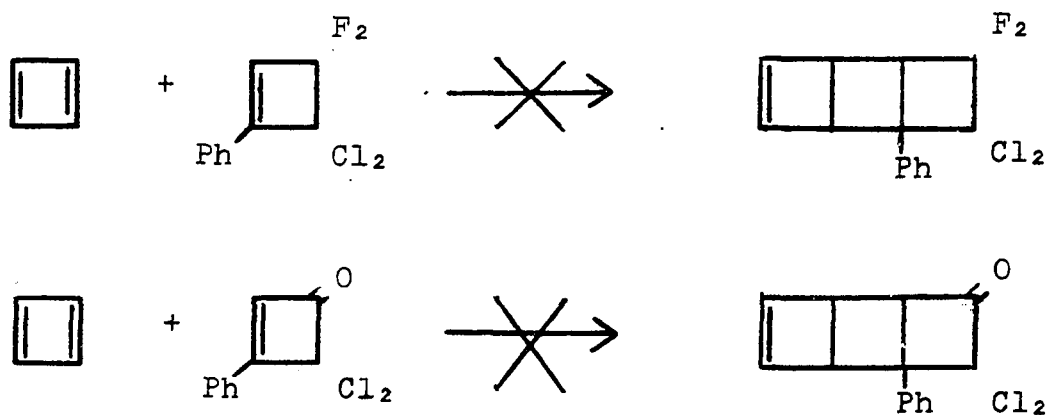


proved quite variable. Dehydrobromination of 52 with potassium t-butoxide in dimethyl sulfoxide did yield a diene 53a or 53b that could be brominated with N-bromosuccinimide; however, difficulties encountered in the preparation of 49 caused the abandonment of the project. Also, it is likely



that triene diketal obtained would upon acid hydrolysis rearrange or fragment rather than give the desired cyclooctatrienedione.

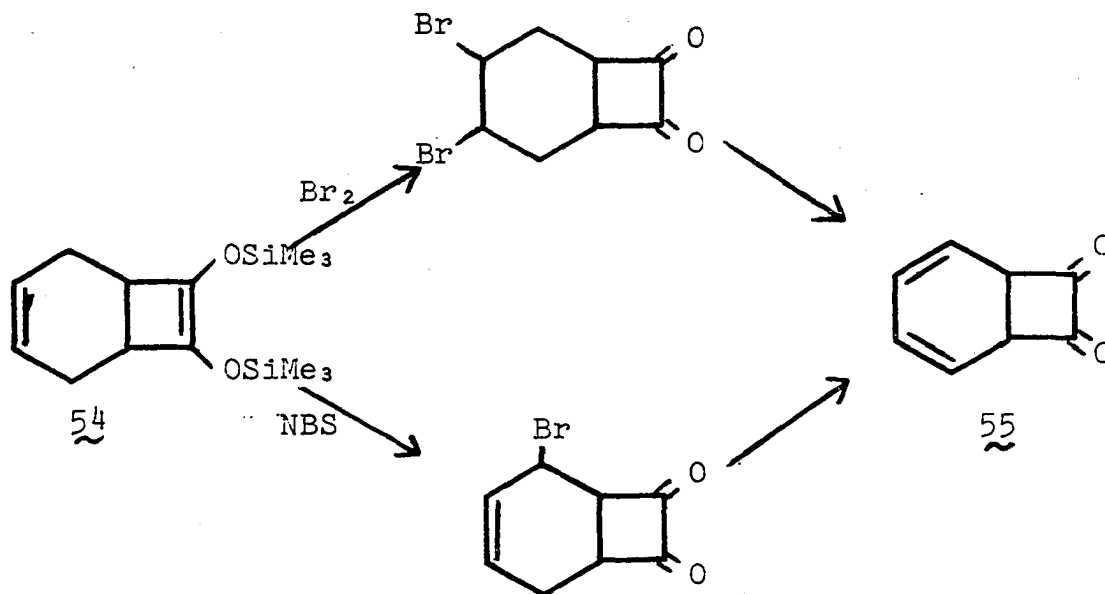
Kowar (80) has also worked toward the synthesis of cyclooctatriene-1,2-dione or its valence isomers. Attempted cycloadditions of cyclobutadiene to substituted cyclobutenes proved unsuccessful in that the cyclobutadiene dimerized to



the total exclusion of any cyclobutene cycloadduct formation.

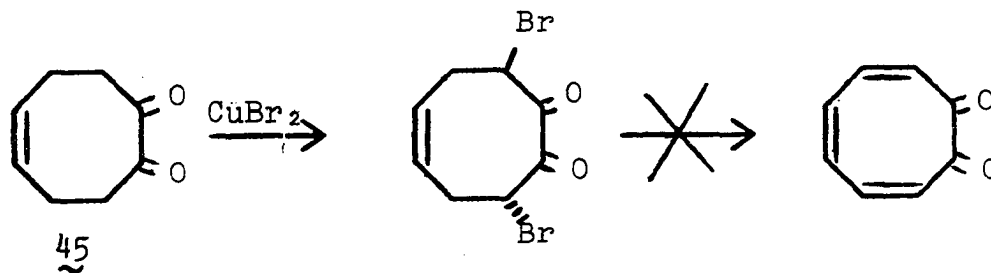
Bromination studies on 7,8-bis(trimethylsiloxy)bicyclo-[4.2.0]octa-3,7-diene 54 did not lead to the desired bicyclo-[4.2.0]octa-2,4-diene-7,8-diene 55 (Scheme 3). Instead,

Scheme 3

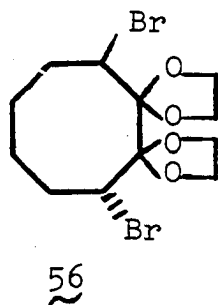


benzocyclobutenedione was the isolated product (80).

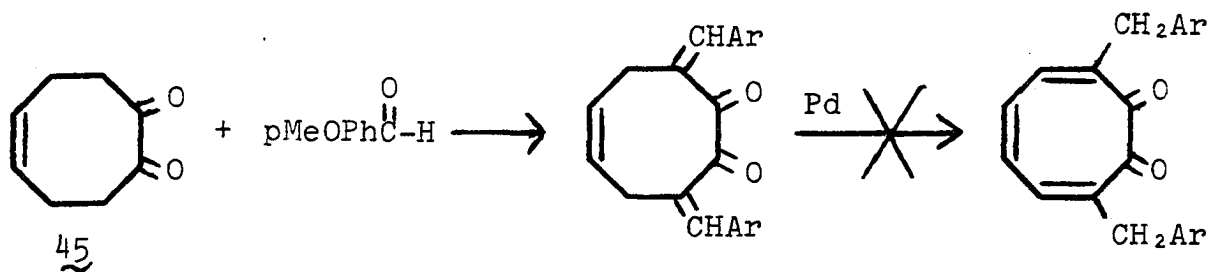
Kowar, unlike Yates, was able to attain α -bromination of 5-cyclooctene-1,2-dione through the use of cupric bromide as the brominating agent; however, all attempts at



dehydrohalogenation were unsuccessful. Also, efforts to produce the dibromo, diketal **56**, by bromination of the diketal or by ketal formation from the dibromide did not bear fruit.



A novel approach to the system was undertaken by Kowar via the formation of an α,α -dimethylene derivative of 45 and p-anisaldehyde; however, attempts at isomerization with



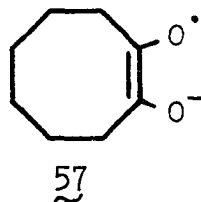
palladium failed, and the desired cyclooctatriene-1,2-dione is still unknown.

DISCUSSION AND RESULTS

The Discussion will center on eight membered cyclic semidiones and their precursors, organized on the basis of degree of unsaturation ranging from cyclooctane semidione to cyclooctatriene semidione. Numerous references will be made to the excellent work of Whittle on bicyclic semidiones (81).

Cyclooctane Semidione

Cyclooctane semidione 57 has been observed by Russell



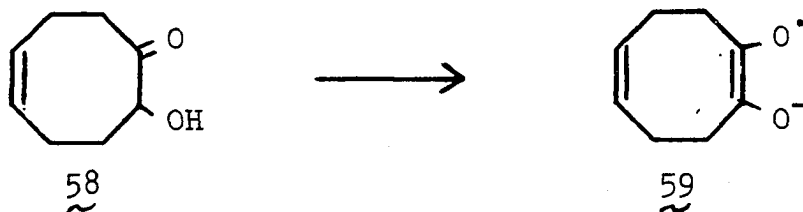
and Strom (82) and by Lown (83), and its esr spectrum consists of four equivalent hydrogen atoms at room temperature, $a^H = 3.336$ (DMSO) and $a^H = 3.456$ (DME). Heating of the DME solution to 88° results in no change in the spectrum; however, upon cooling the solution to temperatures below 14° , additional fine structure appears until -35° when eight clearly resolved lines are formed, $a^H = 4.47$ G (3H) and $a^H = 2.35$ G (1H). Thus, at -35° , there is a freezing out of an asymmetrical conformation. There may still be conformational interconversion occurring at this temperature, but on

the time scale of $\sim 10^{-7}$ sec the four α -hydrogen atoms do not become equivalent. At 25° the conformational interconversions are rapid enough to establish a conformational equilibrium making all four hydrogens equivalent.

It is interesting to note that in both cycloheptane semidione (83) and cyclononane semidione (84), it is possible to differentiate between the quasi-equatorial and the quasi-axial hydrogens at room temperature. Indeed, it was not until 86° and 58° , respectively, that all four α -hydrogen atoms are seen as equivalent. Thus, the rate of conformational interconversion for cyclooctane semidione is much greater than for its next higher or lower homologs.

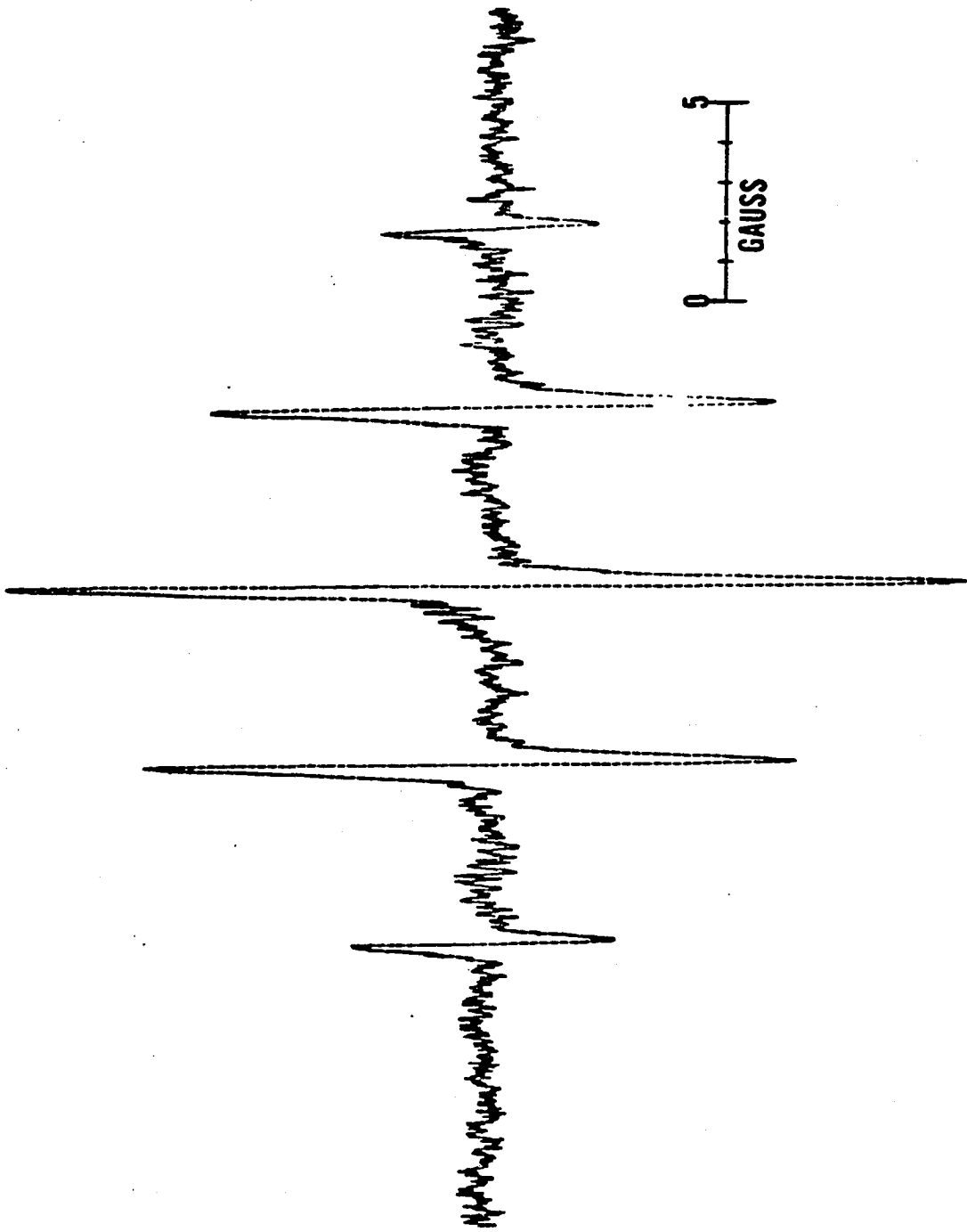
Cyclooctene Semidione

The esr spectrum of 5-cyclooctene-1,2-semidione 59 (Figure 2), produced by treatment of the acyloin 58 with



potassium t-butoxide in DMSO, consists of four equivalent hydrogen atoms, $a^H = 4.5$ G. The equivalency of the α -hydrogens indicates that conformational interconversions are occurring rapidly, and a time averaged spectrum is observed. Thus, the introduction of a double bond in the 5-position

Figure 2. The first derivative esr spectrum of 5-cyclooctene-
1,2-semidione (59) in DMSO



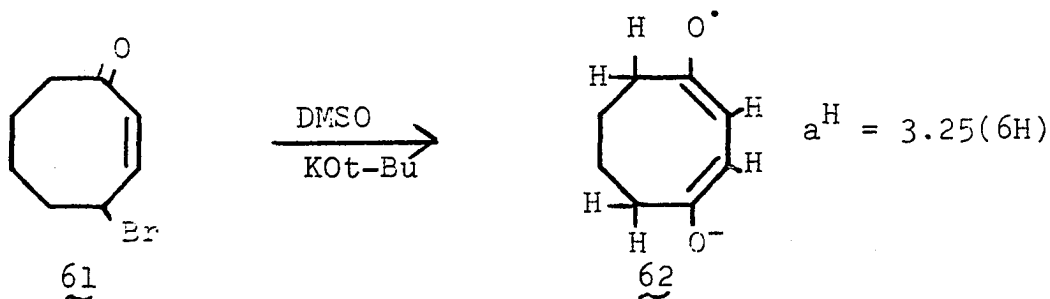
in the eight membered ring does not reduce the conformational mobility of the system at room temperature relative to the saturated case.

Trahanovsky (85), upon treating with potassium t-butoxide the crude reaction mixture from the BF_3 catalyzed oxidation of the cyclooctene oxide 60 with DMSO, obtained a



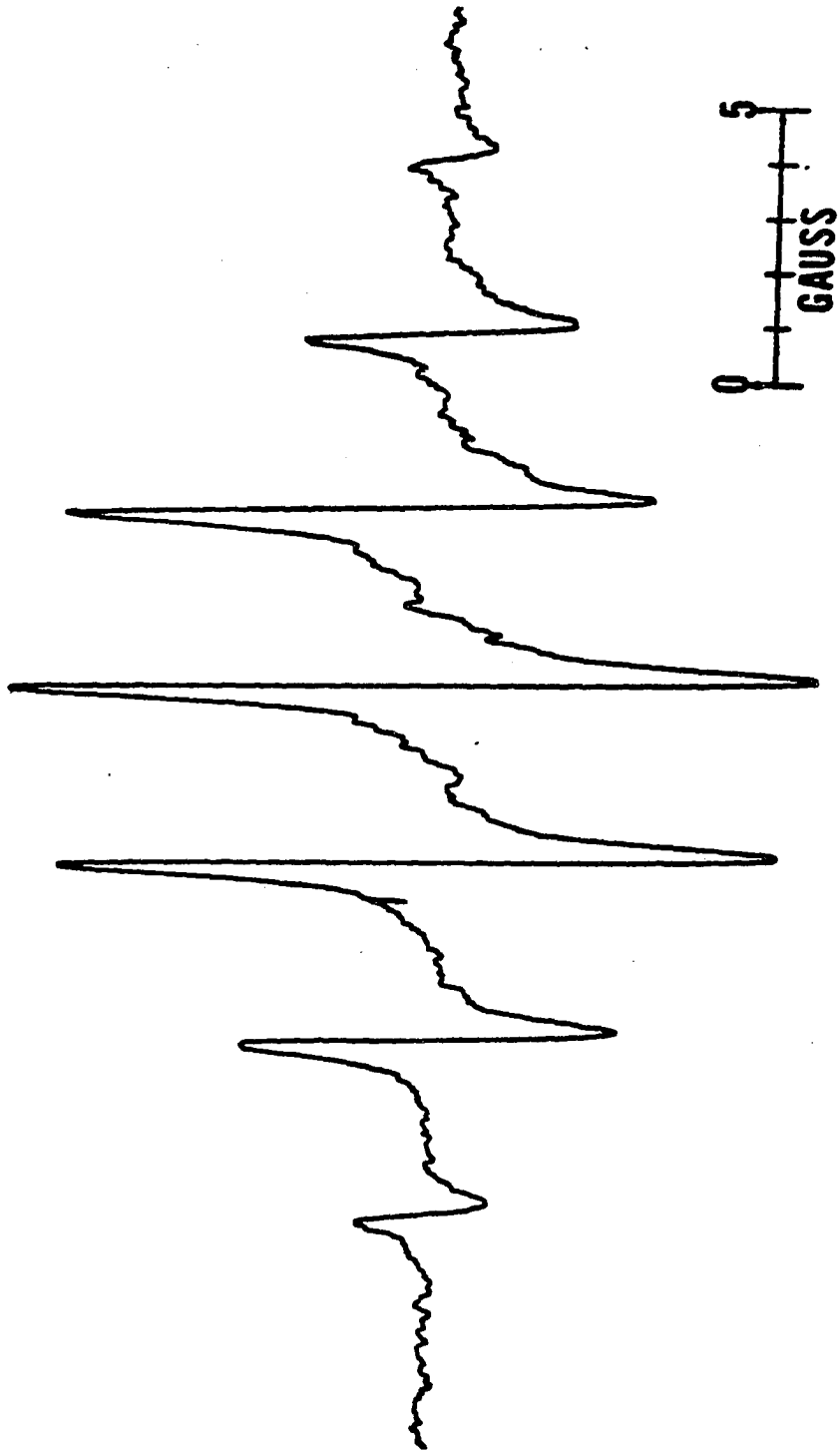
signal that consisted of a triplet with splitting of 3.8 G with considerable broadening probably due to unresolved small splittings.

In cyclooctane, a 1,4 semidione is also possible in which the spin label is spread over four carbon atoms instead of two. Indeed, when 4-bromocyclooct-2-en-1-one is treated with basic DMSO, cyclooct-2-ene-1,4-semidione 62 is observed

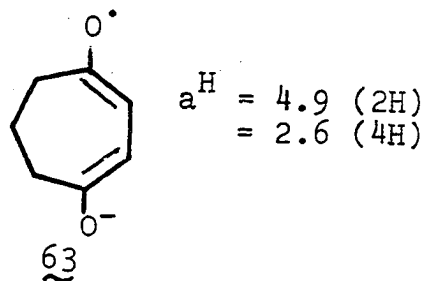


(Figure 3). The magnetic equivalence of all six hydrogen atoms is fortuitous. The time averaging of the α -hydrogen

Figure 3. The first derivative esr spectrum of cyclooct-2-ene-1,4-semidione (62) in DMSO

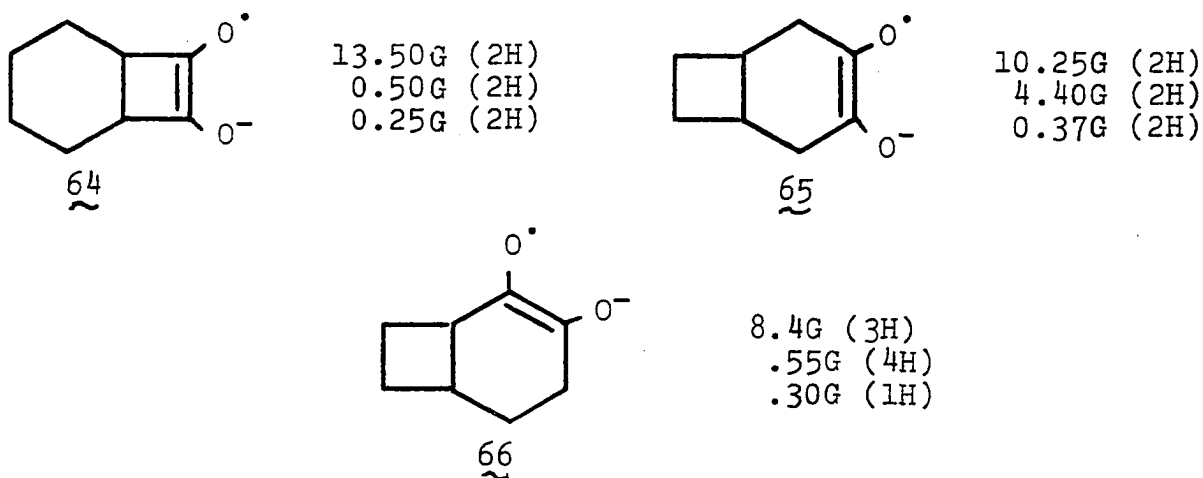


atoms indicates a rapid flipping of the radical anion, as is

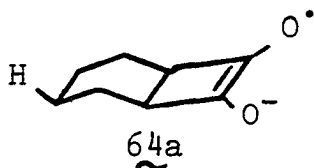


observed in cyclohept-2-ene-1,4-semidione 63 (86).

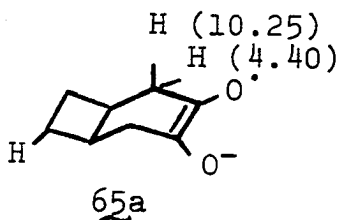
In the bicyclo[4.2.0]octene series, three 1,2-semidiones 64, 65, and 66 are possible. The first two, 64 and 65, were observed by Whittle (81). The large hyperfine splitting



in 64 is assigned to the bridgehead hydrogens and are typical of cyclobutane semidiones. The other assignments are based on conformation 64a with coupling by two of the β -hydrogens and



the two exo hydrogens at C-3 and C-4. Based on the same type of conformation, the assignments for 65 can be made as shown in 65a.



In 66 the large hfsc (Figure 4 and Figure 5) are assigned to the α -hydrogens. The equivalence of the hydrogen atoms at C-4 suggests that the six-membered ring is quite planar with a dihedral angle for the α -hydrogens intermediate between those observed for the axial hydrogens ($a^H = 13.2$ G) and the equatorial hydrogens ($a^H = 6.6$ G) in cyclohexane semidione (87). The assignment of the 0.55 G hfsc is made to the hydrogens at C-5 (exo and endo), C-6, and C-8 (exo). The smallest hfsc is attributed to H-8 (endo) in analogy to semidiones in the bicyclo[3.2.0] system (81).

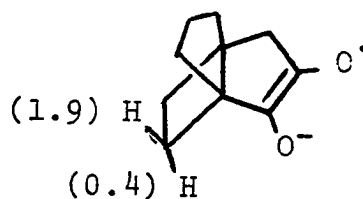
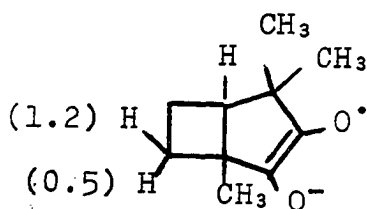


Figure 4. The first derivative esr spectrum of bicyclo[4.2.0]octane-2,3-semidione (66) in DMSO

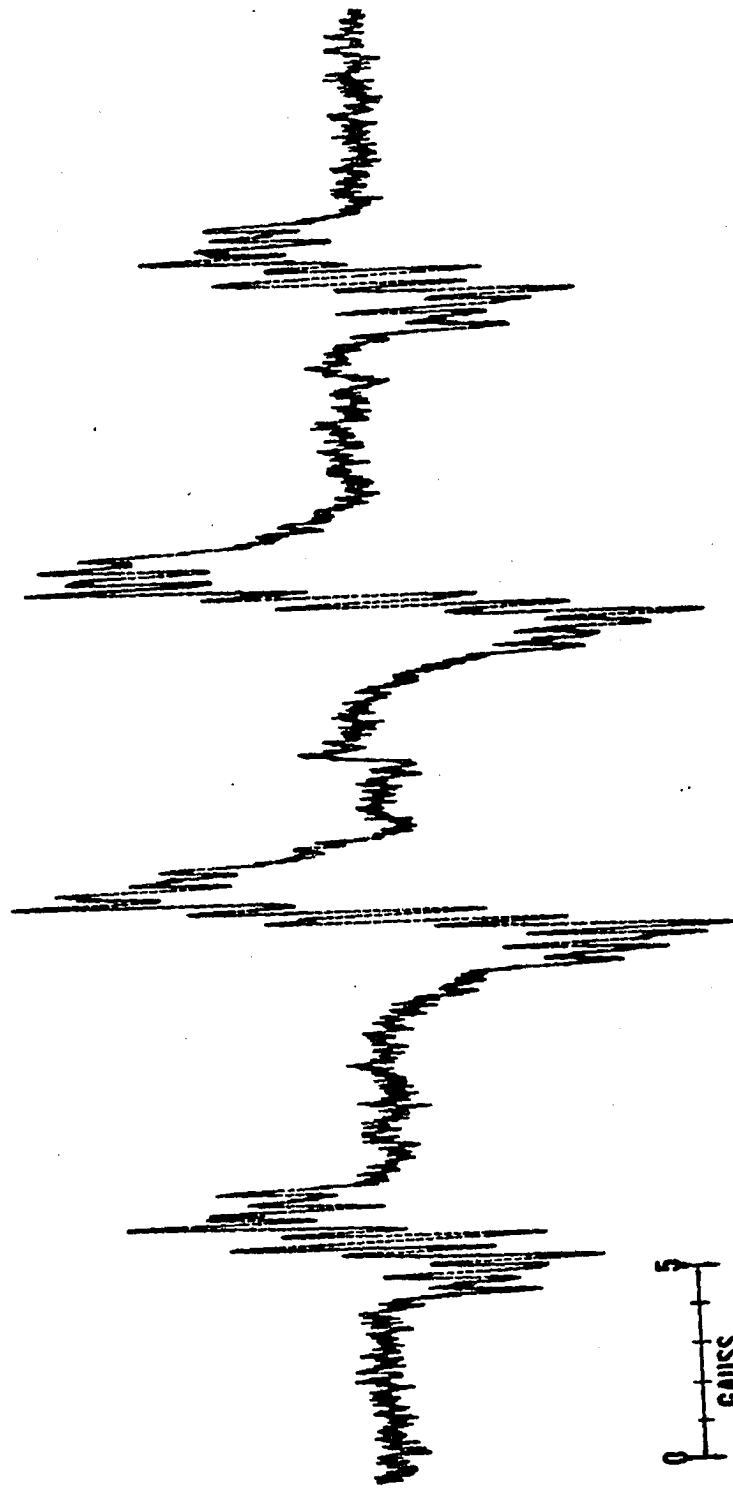
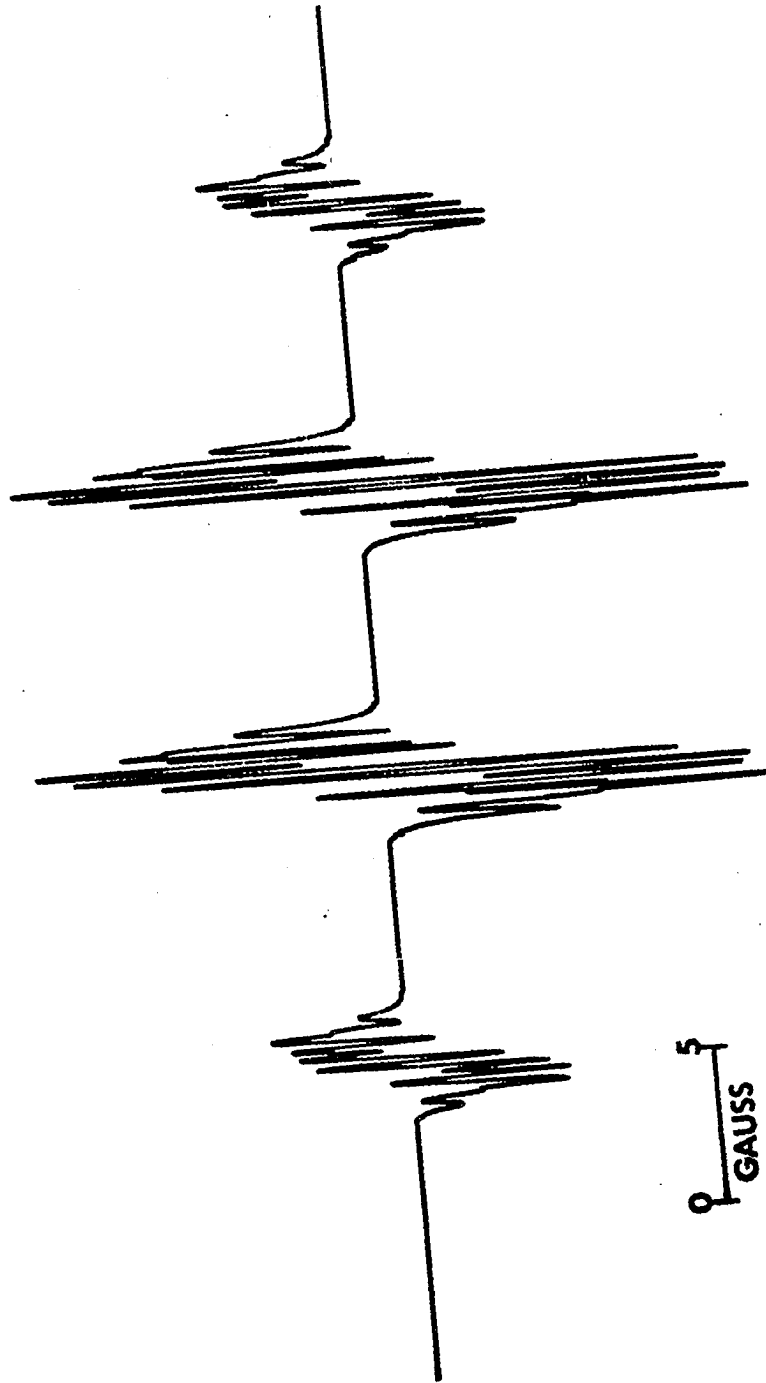
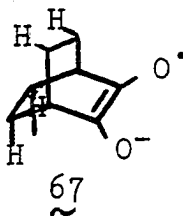


Figure 5. The calculated spectrum of bicyclo[4.2.0]octane-
2,3-semidione (66) for Lorentzian line width
0.1 gauss and splitting constants from text
performed by JEOLCO JNM-RA-1 spectrum accumulator



The semidione of bicyclo[2.2.2]octane 67 is well studied and shows a quintet splitting of 2.09 G assigned to the

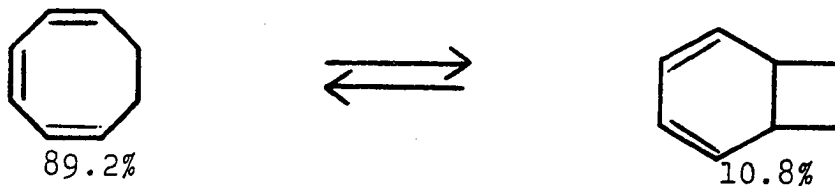


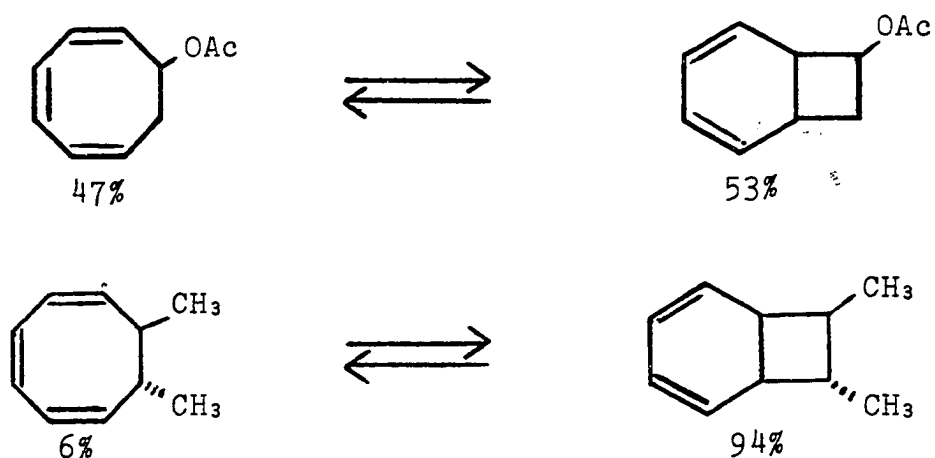
anti-hydrogens at C-5, 6, 7, and 8 (88). The α -hydrogens are not seen because they are perpendicular to the semidione π system, and, thus, the dihedral angle is 90° .

Cyclooctadiene and Cyclooctatriene Semidiones

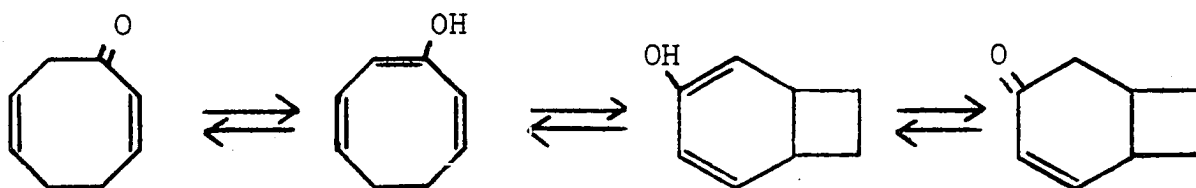
The cyclooctadiene and cyclooctatriene semidione series and their possible precursors will be considered as a unit for reasons to be discussed later.

Introduction of added degrees of unsaturation in the system opens up new possibilities for rearrangements. Indeed, 1,3,5-cyclooctatriene exists in equilibrium with its bicyclic isomer; the percentage of bicyclic isomer present is dependent upon substitution. For example, at 60° (25),





Also, Farrissey and Perry observed the rearrangement of 2,6-cyclooctadien-1-one to bicyclo[4.2.0]oct-4-en-3-one upon

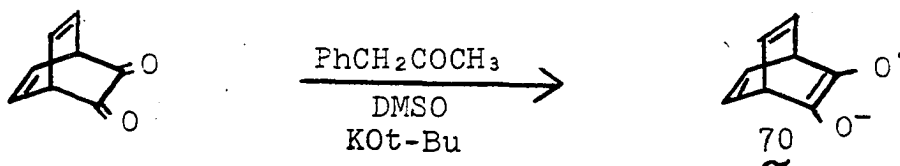


thermolysis, presumably via an enol intermediate (89). The rearrangements of cyclooctatetraene were discussed previously.

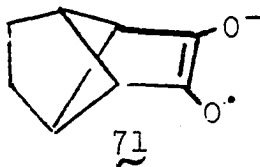
In the bicyclo[4.2.0]octene semidione series, Whittle has found that bicyclo[4.2.0]oct-3-ene-7,8-semidione **68** exhibits an α splitting typical of substituted cyclobutane semidiones (13.50 G) along with $a^H = 0.6$ G (2H) and $a^H = 0.35$ G (2H), the latter assigned to the vinylic hydrogens (81).



The bicyclo[2.2.2]octene semidione 69 was found by Russell and co-workers (90) to be a very stable radical, and, as expected, the bridgehead hydrogen atoms were not seen. A hfsc of 2.60 G was assigned to the exo hydrogens at C-7 and C-8 with the olefinic and endo hydrogens exhibiting the identical hfsc's of 0.41 G. Despite the stability of 69, attempts to generate bicyclo[2.2.2]octa-5,7-diene-2,3-semidione 70 from the corresponding diketone with basic DMSO and propiophenone proved unsuccessful even under flow conditions.

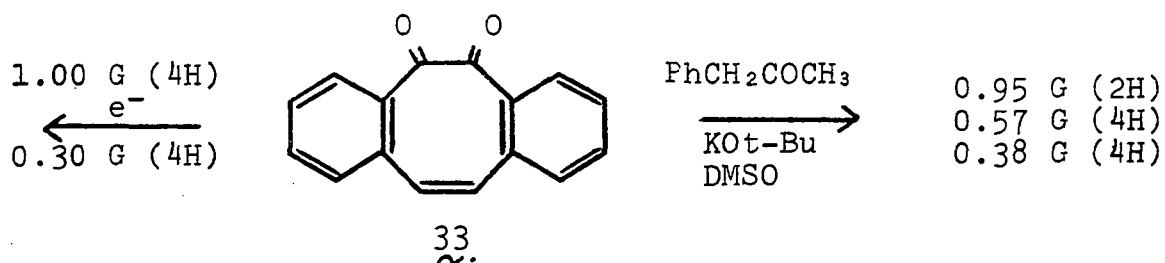


The study of tricyclo[3.3.0.0^{4,8}]octane-2,3-semidione 71 by Whittle (81) was complicated by its instability and by the appearance of another complex signal superimposed upon the desired spectrum. However, it was possible to discern the spectrum of the desired radical from the initial spectra of three reactions with the following hfsc's and assignments



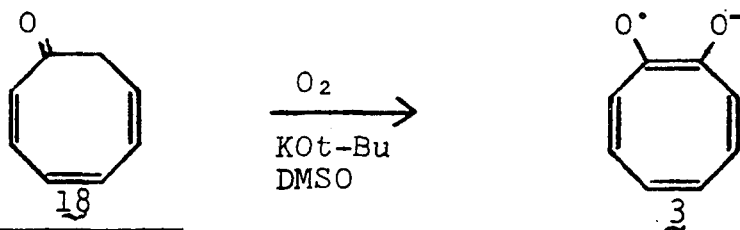
(0.80 G, H-5 and H-8; 0.20 G, H-1 and H-4; and 0.15 G, H-6 and H-7).

In the cyclooctatriene semidione series, one known precursor is the dibenzotrienedione previously mentioned, 33. The presence of the two fused benzo groups should cut down on the rearrangements of the semidione and also have a stabilizing influence. However, two distinct signals are obtained upon treatment with basic DMSO and propiophenone (85) or upon electrolytic reduction¹, respectively. Thus far, the



discrepancy between the two signals obtained has not been resolved.

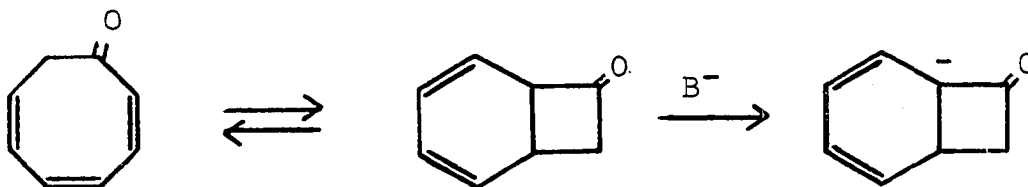
In an attempt to produce the unsubstituted cyclooctatriene-1,2-semidione 3, Gund (77) and others treated 2,4,6-cyclooctatriene-1-one 18 with KOt-Bu and DMSO in the presence of O₂ both under static and flow conditions, as this mixture



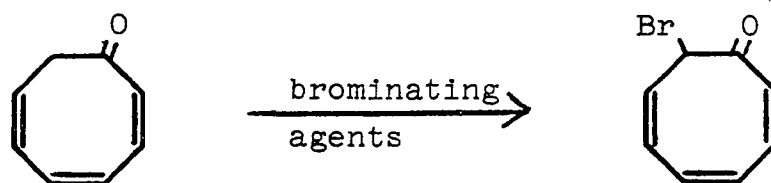
¹R. L. Blankespoor, Unpublished results, Iowa State University, 1972.

is known to oxidize ketones with α -methylene groups to semidiones; however, no definable radical was obtained. Thus, began the long and painful search for an α substituted trienone derivative that would serve as a precursor to cyclooctatriene semidione or its isomers.

The many endeavors in search of the parent cyclooctatrienedione have been discussed. Attempts to direct α substitution of the trienone have proved unsuccessful presumably due to the compound's reluctance to enolize and its sensitivity to acid and base. Indeed, Cope and co-workers (91) were unsuccessful in attempts to generate the cyclooctatrienone anion as the α -bridgehead hydrogen of the bicyclo[4.2.0] form proved most acidic.



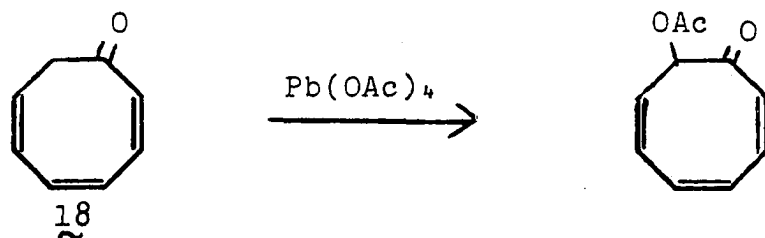
Bromination studies conducted by Gund (77) gave tars,



aldehydes, and aromatic bromides instead of the desired α -bromide. Also, the treatment of 18 with trimethylene thiosylate, a reagent found to be excellent for oxidation

of active methylene groups to the dithiane which can be oxidized by mercuric salts to the diketone (92), proved unsuccessful.

Oxidation of 18 with lead tetracetate did not lead to



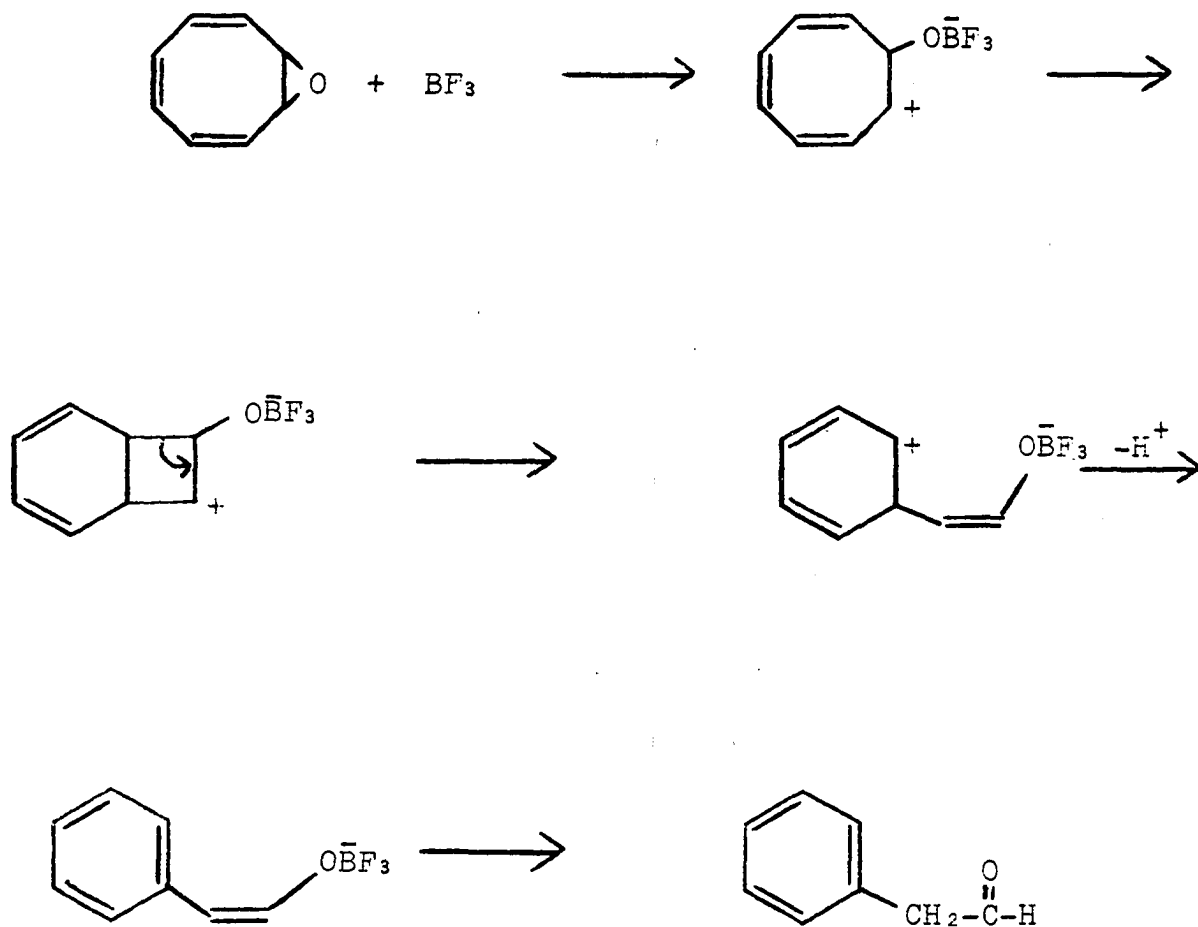
normal product, the α -acetoxy ketone, but instead generated phenyl acetic acid².

The boron trifluoride catalyzed DMSO oxidation of cyclooctatetraene oxide proceeded to phenylacetaldehyde instead of the hydroxy ketone (77). This rearrangement is not surprising

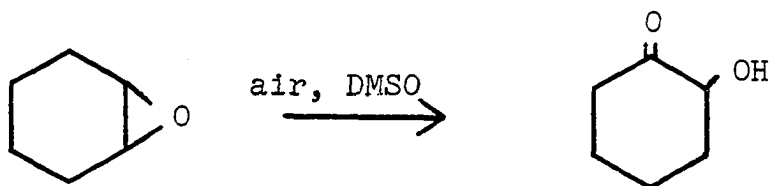


as the acid catalyzed oxidation would proceed via a carbonium ion mechanism inviting rearrangement.

²L. A. Ochrymowycz, Private communication, Iowa State University, 1969.



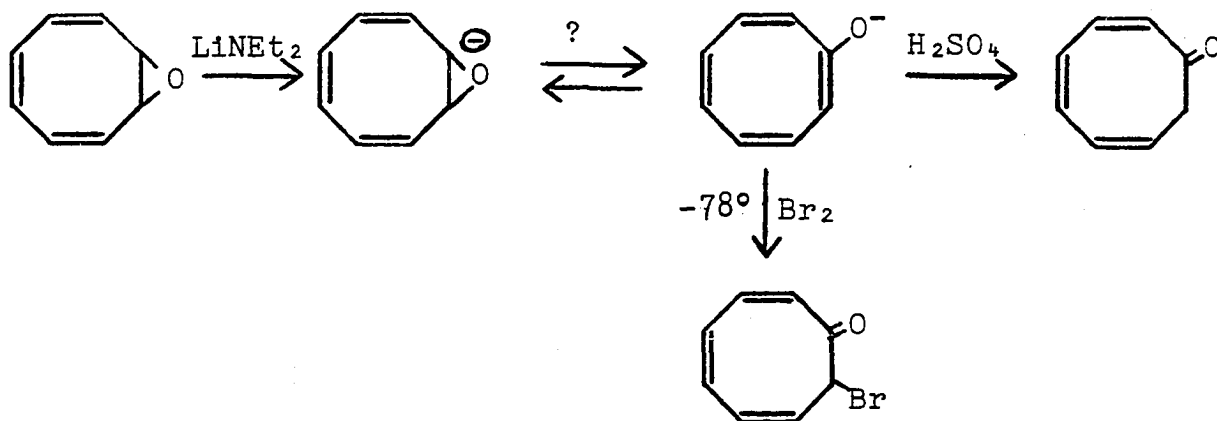
Tsuji (93) was able to attain the air catalyzed DMSO oxidation of cyclohexene oxide to 2-hydroxycyclohexanone and postulated a radical mechanism. Also, Oda and co-workers (94)



achieved this oxidation using pyridine-N-oxide as the oxidizing agent, an unlikely carbonium ion process. However,

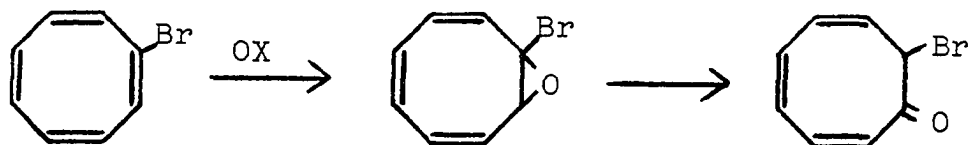
neither method resulted in the oxidation of cyclooctatetraene oxide. The starting material was recovered unchanged from both reaction mixtures even when pure oxygen was bubbled through the DMSO solution.

Recently, Stotter and Hill (95) have developed a convenient procedure for the preparation of α -bromo ketones, prime semidione precursors, by the low temperature bromination of lithium enolates. Because the enolate of cyclooctatrienone cannot be generated directly from the ketone, the epoxide seemed a likely precursor since the trienone was synthesized in good yield from the treatment of the epoxide with base followed by acidic work-up. This bromination procedure gave

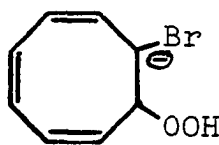


a yellow solution (CH_2Cl_2), which upon concentration gave a brown tar. In an attempt to avoid isolation of the neat product, DMSO was added to the methylene chloride solution, and CH_2Cl_2 was distilled away. However, this DMSO solution blackened upon standing, and no definable esr signal was obtained upon treatment with KOtBu even under flow conditions.

Monosubstituted cyclooctatetraene derivatives can also be considered as possible intermediates in route to the semidione. In fact, oxidation of halogen substituted olefins with peracids often results in the production of haloketones by initial formation of a haloepoxide and subsequent rearrangement (96). However, a halogen substituent tends to deactivate a double bond toward peracid oxidation compared to unsubstituted double bonds, and, thus, successful oxidation of bromocyclooctatetraene with peracids was deemed unlikely.

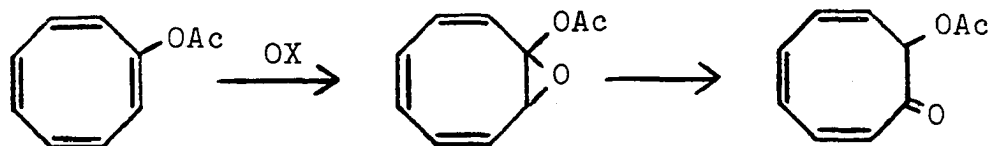


On the other hand, attack by basic hydrogen peroxide should be more favorable due to the inductive effect of the bromine, but only tars resulted when basic hydrogen peroxide was allowed to react with bromocyclooctatetraene.



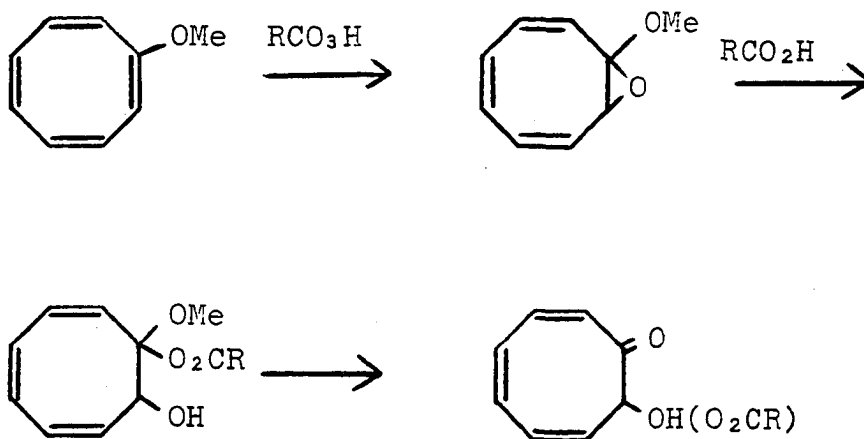
The epoxidation of enol acetates leads to the formation of epoxy acetates, which undergo either an intramolecular thermal isomerization or an acid catalyzed isomerization to form α -acetoxy ketones (97,98), an ideal precursor to

semidiones. Also, the acetate substituent should activate

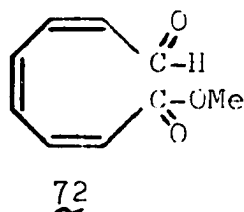


the double bond toward oxidation by peracids. However, under the identical conditions in which cyclooctatetraene oxide was produced from cyclooctatetraene (m-chloroperbenzoic acid at -30°), there was no evidence of reaction. Heating the reaction mixture or use of a stronger oxidant (trifluoroperacetic acid) resulted in destruction of starting material with none of the desired epoxy acetate or acetoxy ketone produced.

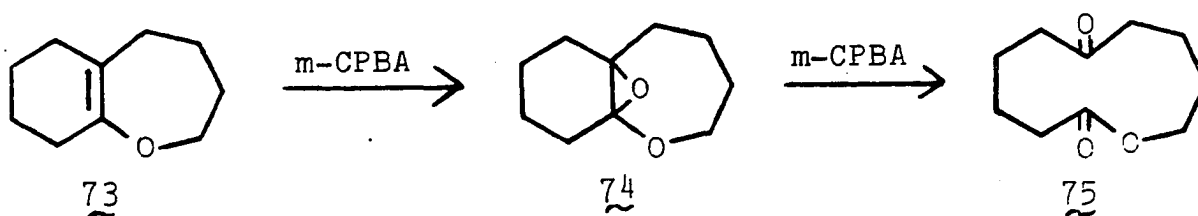
Enol ethers quite readily undergo oxidation with peracids to give an epoxy ether which usually reacts with the acid generated in the reaction mixture to give a hydroxy ketone derivative (99,100). Indeed, the reaction between



methoxycyclooctatetraene and *m*-chloroperbenzoic acid was quite facile. However, the crystalline product formed appeared by mass spectral and nuclear magnetic resonance data to be acyclic aldehyde-ester 72. This reaction is not without

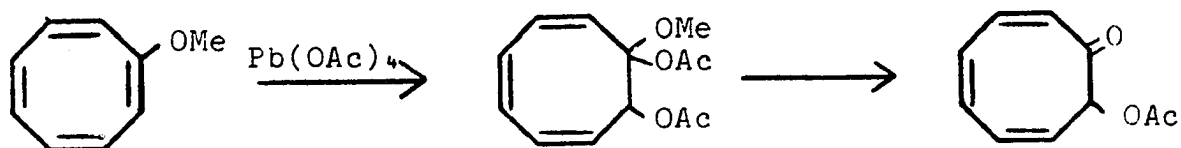


precedent in that the bicyclic enol ether 73 was seen to open up to the keto lactone 75 upon oxidation (101). Use of a



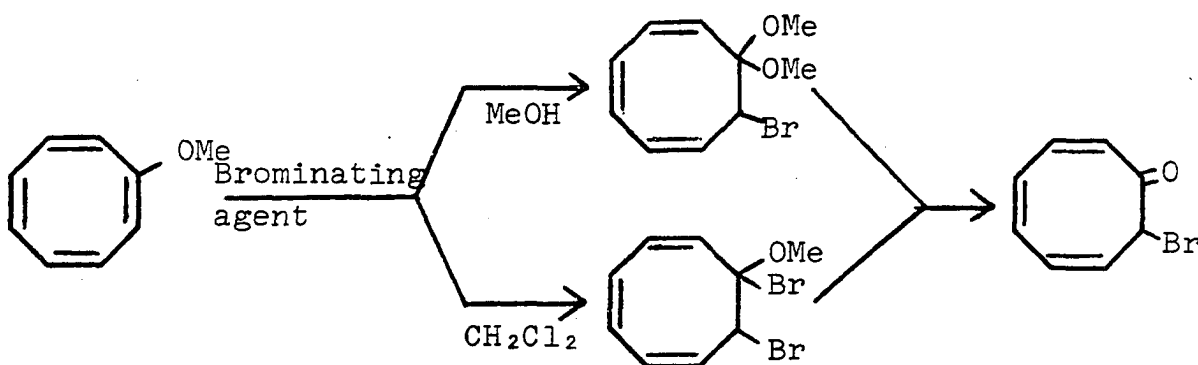
stronger and less nucleophilic peracid (trifluoroperacetic acid) resulted in hydrolysis of the enol ether to the ketone with no evidence of oxidation.

Since the lead tetraacetate oxidation of ethoxyethylene gave acetoxyacetaldehyde in good yield (102), the oxidation of methoxycyclooctatetraene was attempted in the hopes of



obtaining the corresponding acetoxy ketone. The oxidation gave a complex mixture of products without significant acetoxy group incorporation. The esr spectrum obtained upon treatment of this crude mixture under static conditions with KOt-Bu and DMSO is of interest only in its complexity with over 150 lines discernible (Figure 6).

Also, bromination studies on the methoxycyclooctatetraene in both aprotic and alcoholic solvents utilizing molecular



bromine, pyridinium bromide perbromide, and cupric bromide were also unsuccessful.

Bromination studies on cyclooctatetraene itself using DMSO as the solvent in attempt to take advantage of its oxidizing ability gave only tars. Indeed, dissolution of

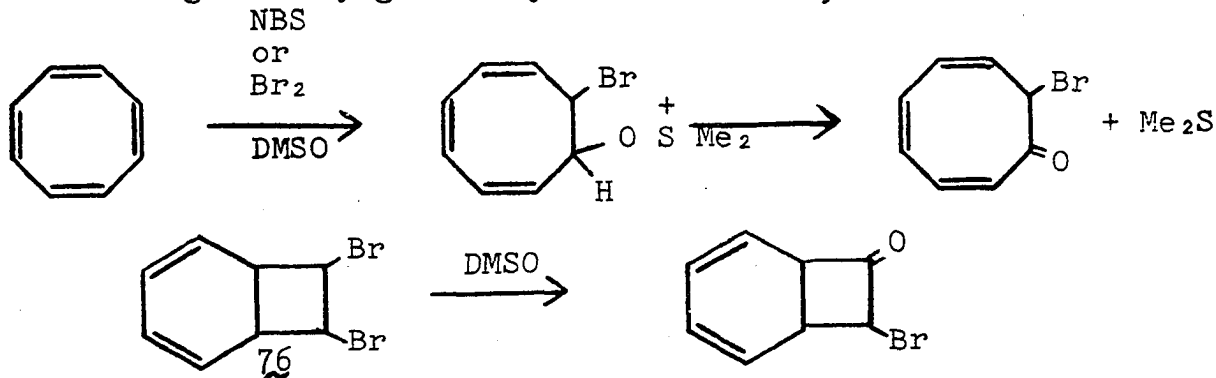
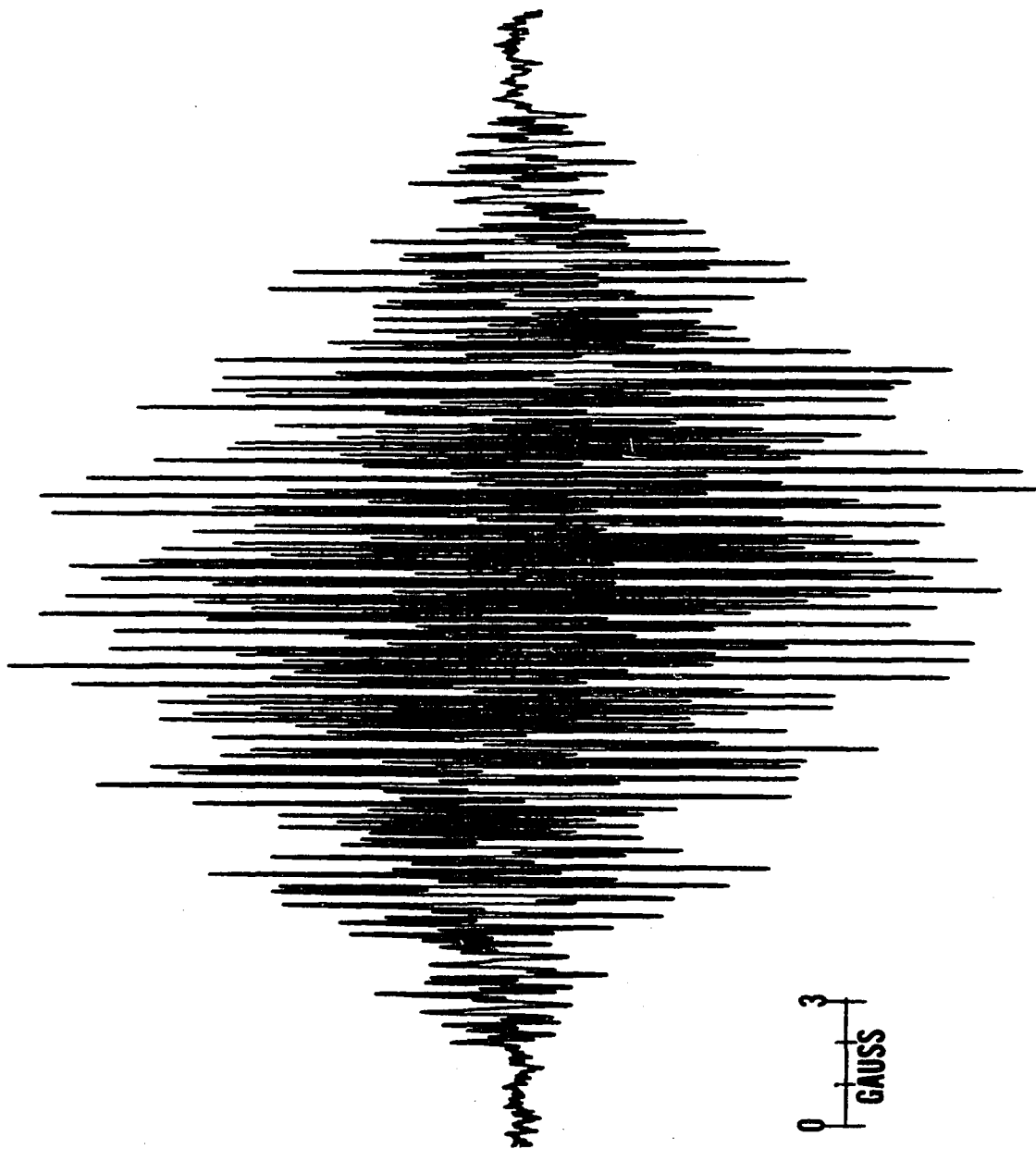


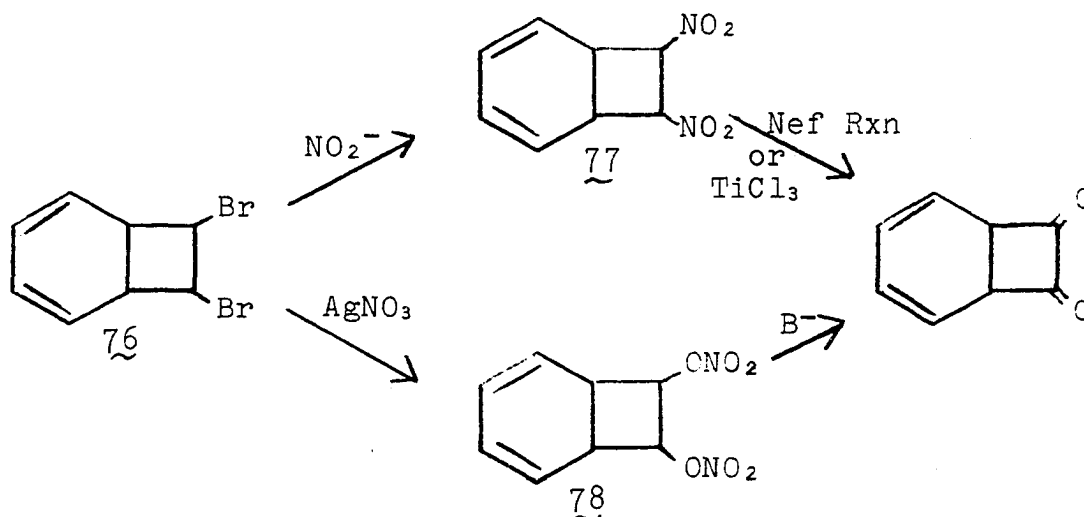
Figure 6. The first derivative esr spectrum of the radicals obtained in DMSO from the crude product of the lead tetracetate oxidation of methoxycyclooctatetraene



7,8-dibromobicyclo[4.2.0]octa-2,4-diene 76, which is the product obtained upon the addition of one mole of bromine to cyclooctatetraene, in DMSO resulted in tar formation.

Attempts to minimize tar formation by the addition of NaHCO_3 to neutralize the HBr generated or by the addition of Ag^+ to assist in the removal of the Br^- proved negative.

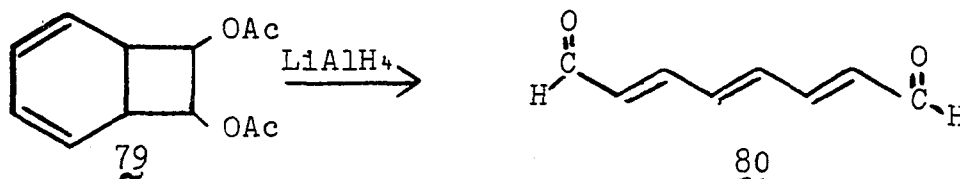
Efforts were undertaken on the substitution of a nitro group or a nitrate ester for bromide in 76. The nitro compound 77 could then be oxidized to the diketone by the Nef



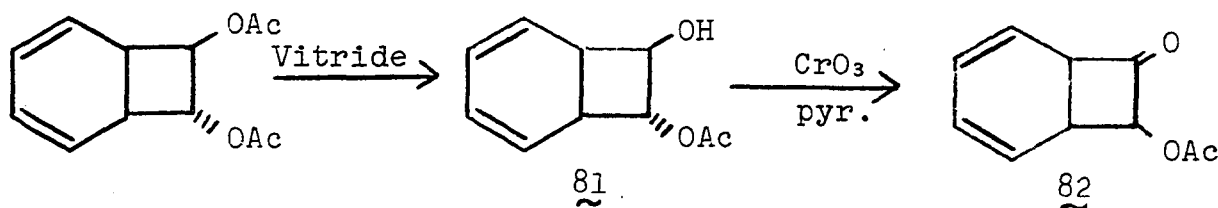
reaction (103) or more likely by treatment with titanium trichloride (104). The nitrate ester upon treatment with base could undergo an α elimination to the diketone (105). However, neither substitution reaction was successful.

One substitution reaction on 76 that proceeds cleanly without skeletal rearrangement is the replacement of bromide with acetate. Indeed, this can be accomplished with either

NaOAc or AgOAc in acetic acid. Anet (106) has determined that alkaline hydrolysis of the diacetate 79 gives an "intractable material" and that the reduction with lithium aluminum hydride gives as an unexpected product the dialdehyde 80. Since the diacetate has a trans configuration, a



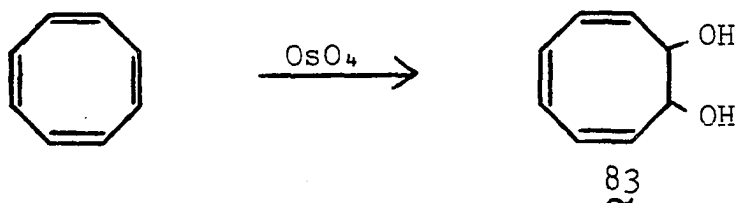
selective reduction of the more exposed exo-acetate group is conceivable if a bulky reducing agent such as Vitride [sodium bis(2-methoxyethoxy)aluminum hydride] is used. Also, Vitride has the advantage of being completely soluble in



benzene so that an inverse addition (reducing agent to ester) could be performed. The resultant hydroxy acetate 81 could then be oxidized with chromium trioxide to the acetoxy ketone 82. The reaction was carried out at approximately -70° as indicated by Vit (107), and followed by a basic work-up similar to that of the Fiesers' (108) for LiAlH_4 reductions. Acidic work-up was avoided to preclude acid catalyzed

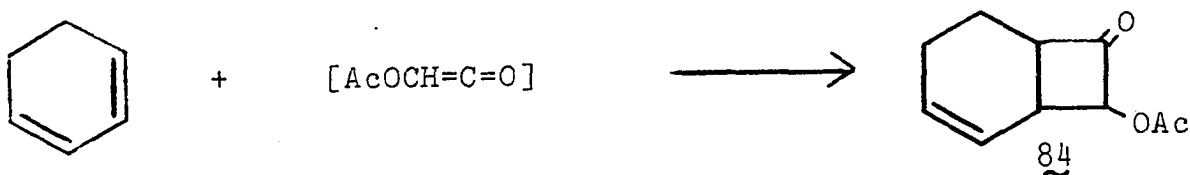
rearrangement. However, both acetate groups were found to have disappeared by nmr analysis with aldehyde formation. Apparently, the basic work-up caused the hydrolysis of the second acetate group with subsequent ring opening. Acidic work-up of the above reaction also gave aldehydic products.

An attempt by Gund (77) to obtain the monocyclic diol 83 directly by the oxidation of cyclooctatetraene by osmium tetroxide proved unsuccessful. The osmium tetroxide

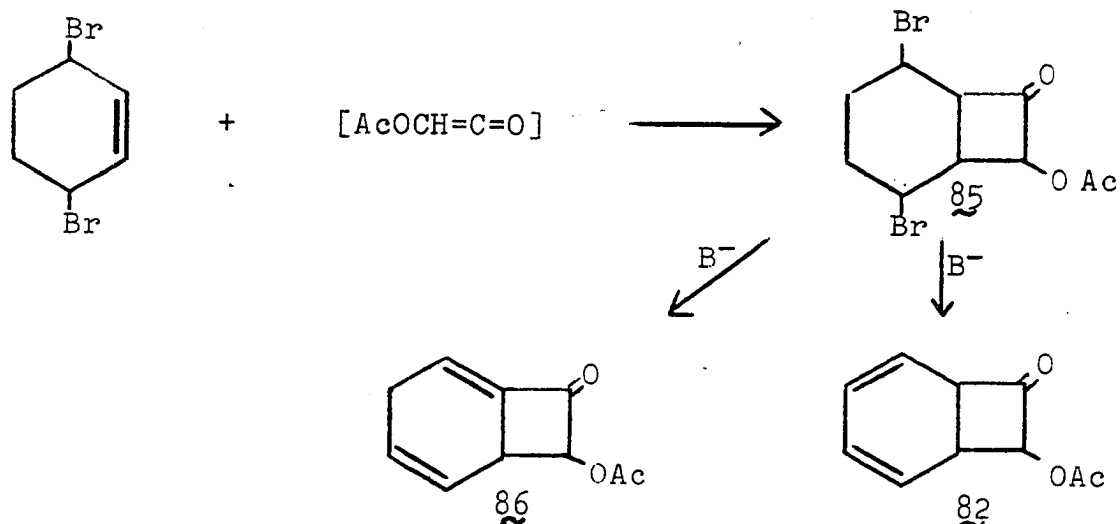


catalyzed oxidation of cyclooctatetraene by hydrogen peroxide in t-butanol gave the acyclic dialdehyde 80.

Trying to approach the desired system through cycloaddition reactions, Schmitt³ generated acetoxyketene in the presence of 1,3-cyclohexadiene, but none of the expected cycloadduct 84 was detected. In a somewhat simplistic

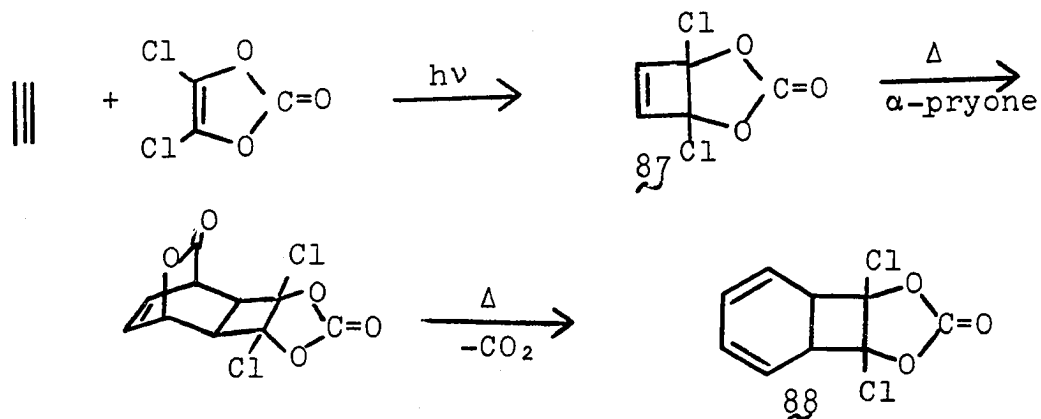


³K. S. Schmitt, Private communication, Iowa State University, 1972.

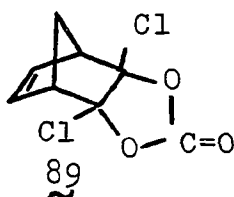


endeavor, the addition of acetoxyketene to 3,6-dibromocyclohexene was attempted but to no avail. Even if the dibromocycloadduct **85** was obtained, the chances of the dehydrobromination with base proceeding to give the desired diene **82** are quite small. Due to the acidity of the bridge-head proton α to the ketone functionality, the diene **86** would most likely be produced.

In a more elaborate scheme, acetylene was added photochemically to dichlorovinylene carbonate (109). If this

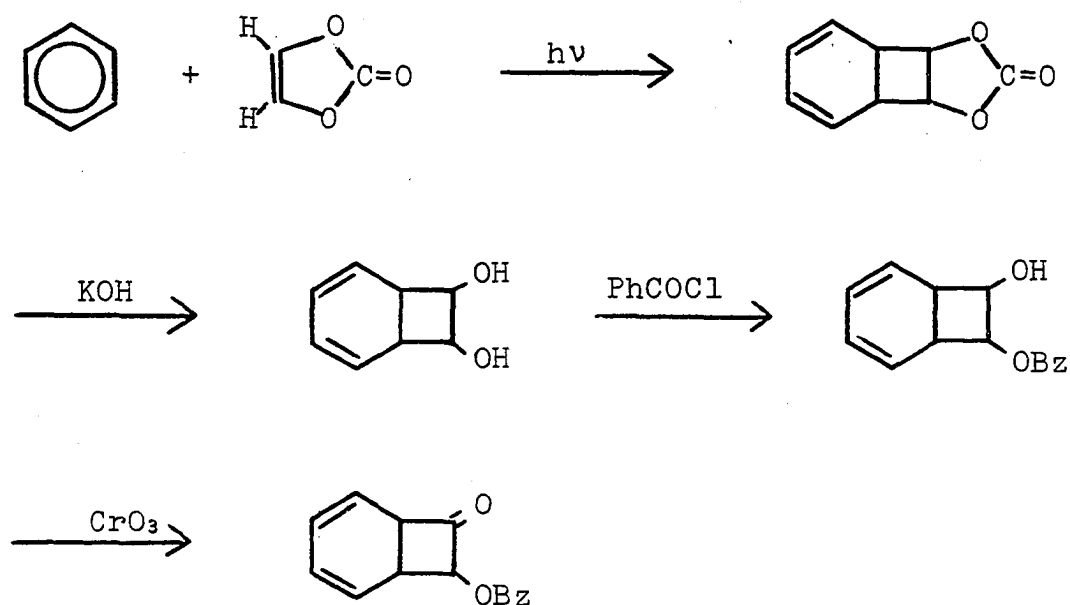


cyclobutene derivative 87 would undergo a Diels-Alder addition with α -pyrone and carbon dioxide could be eliminated thermally from the adduct, a prime dione precursor, the bicyclo dichlorocarbonate 88 would be generated. However, the 1,5-dichloro-2,4-dioxabicyclo[3.2.0]hept-6-en-3-one 87 decomposed thermally before undergoing an addition reaction. Later it was discovered that 88 could be produced directly from the sensitized photoaddition of dichlorovinylene carbonate to benzene (110,111). In situ hydrolysis of 88 with KOt-Bu and DMSO in an esr cell did not result in an observable radical even under flow conditions. There was evidence of reaction of 88 with DMSO as a gas was generated upon dissolution. A similar absence of an esr signal was obtained by Schmitt (6) in the hydrolysis of the bicyclo[2.2.1]heptene derivative 89. Attempted hydrolysis of 88 with aqueous KOH in a two phase

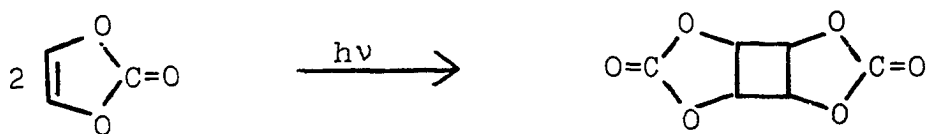


reaction mixture with ether gave a tarry mass as product.

In that the generation of the dione from the dichloro-carbonate was not forthcoming, a sensitized photoaddition of vinylene carbonate to benzene was proposed. The hydrolysis of carbonates with base generally proceeds more cleanly

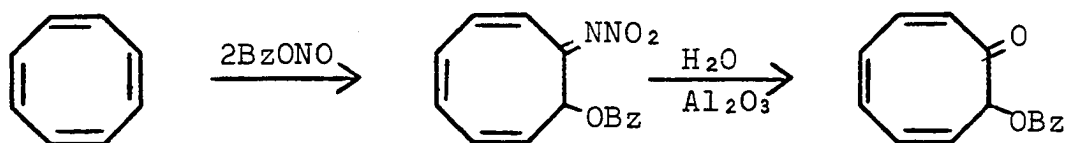


than the dichloro derivative. The diol thus obtained could then be functionalized to the monoester with one equivalent of acid chloride and then oxidized by chromium trioxide to the ketone, a reaction sequence used quite widely and with great success by Schmitt (6). But the photochemical reaction gave only dimer. Indeed, it was later discovered that



Hartman and Steinmetz (112) had conducted dimerization studies on vinylene carbonate in benzene.

Schmitt⁴ also investigated the reaction of cyclooctatetraene with benzoyl nitrite as disubstituted olefins often form α -benzoyloxy nitrimines on reaction with two equivalents of benzoyl nitrite (113). The nitrimine thus formed could be hydrolyzed to the α -benzoyloxy ketone (114), which would be

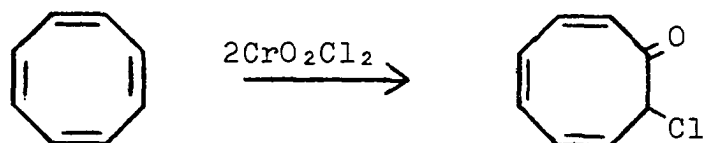


a useful semidione generator. However, cyclooctatetraene was inert to the benzoyl nitrite. The destruction of the benzoyl nitrite resulted when the two were heated together.

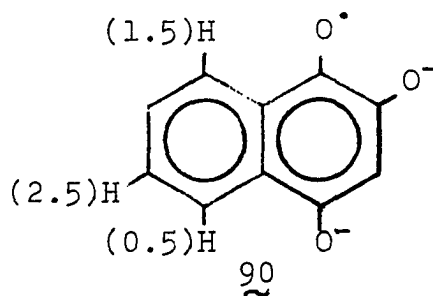
Recently, it was discovered by Sharpless and Teranishi (115) that an olefin could be oxidized by chromyl chloride in acetone to the α -chloro ketone. Although previous oxidations were performed only on monoolefins, the oxidation of cyclooctatetraene was attempted. The somewhat interesting result was obtained in that two equivalents of chromyl chloride were required to effect the oxidation. When one equivalent was used, the cyclooctatetraene was recovered unchanged from the reaction mixture. The crude oxidation product

⁴K. D. Schmitt, Private communication, Iowa State University, Ames, Iowa 1973.

obtained was quite unstable, decomposing upon concentration or upon standing. If this crude product was allowed to react with KOt-Bu in DMSO in the esr cavity, a spectrum was obtained which consisted of a doublet of doublets of doublets

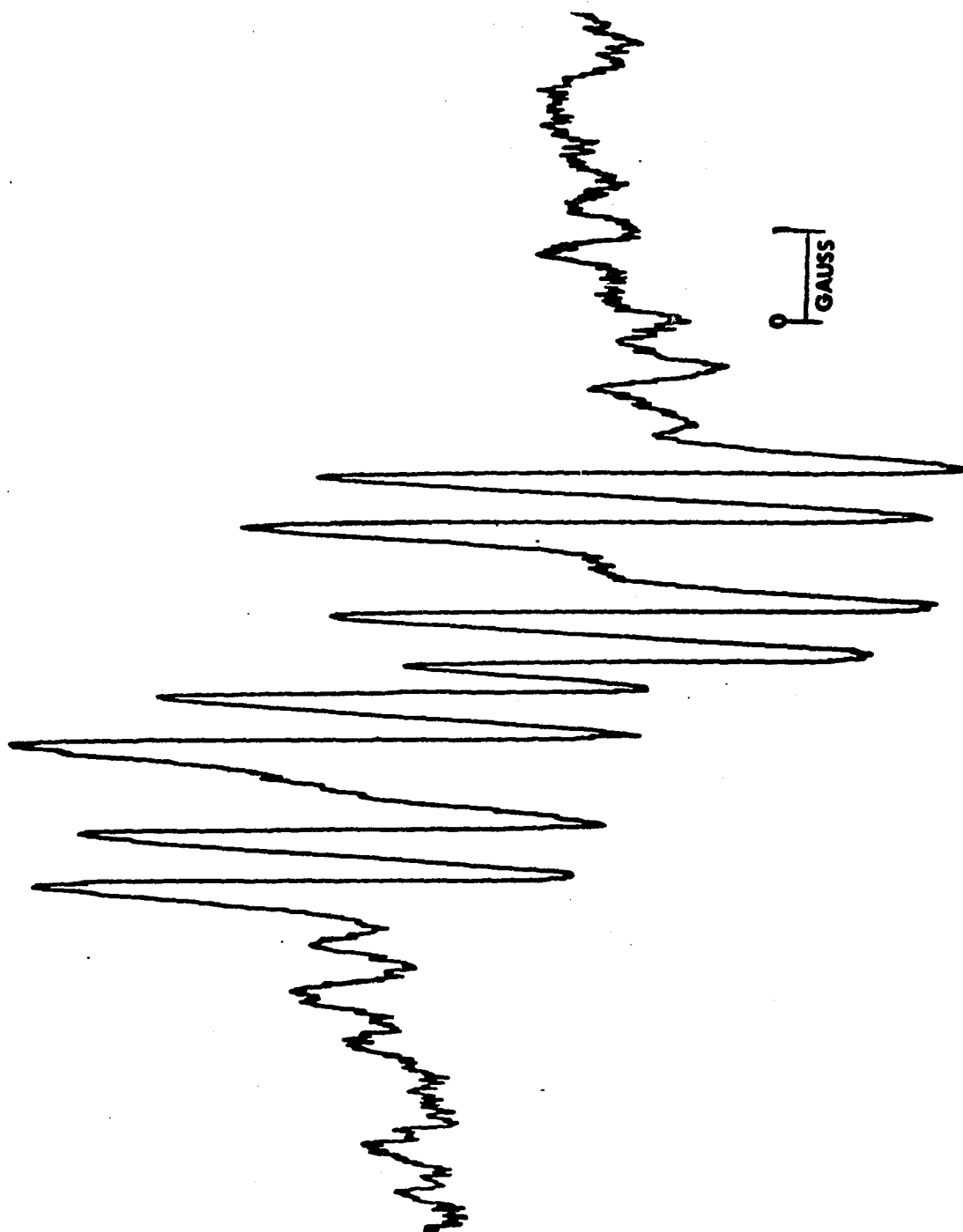


($a^{\text{H}} = 2.56, 1.5 \text{ G}, \text{ and } 0.5 \text{ G}$) (Figure 7). The observed splittings must result from three nonequivalent hydrogen atoms and are quite small. The signal was found to be identical to that of the lawsone radical 90. This radical

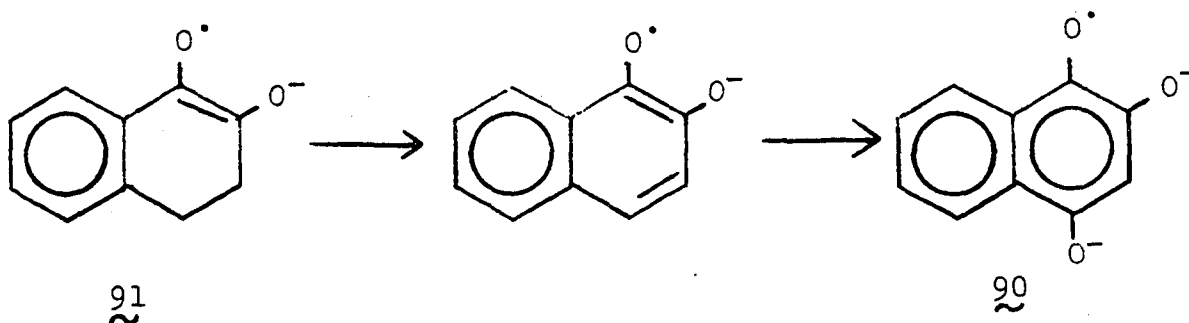


dianion is frequently seen and arises from a great variety of precursors: o-naphthoquinone, α - and β -tetralone, $\Delta^{1,9}$ -3-acetoxy-2-octalone, bullvalone, 4,5-benzocycloheptanone, 2,3-benzo-4-cycloheptenone, 3,4-benzobicyclo[4.1.0]heptanone, and various other ten carbon unsaturated ketone precursors.

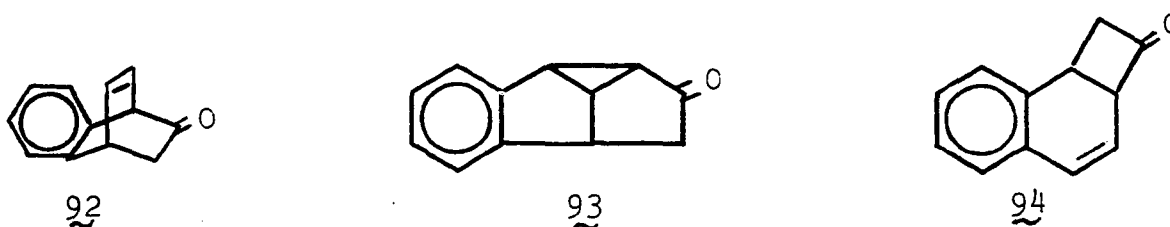
Figure 7. The first derivative esr spectrum of the radical obtained in DMSO from the crude reaction product of cyclooctatetraene and two equivalents of chromyl chloride



It has also been traced back in some cases to 3,4-benzocyclohexene-1,2-semidione 91.



Blankespoor⁵ has observed that treatment of compounds 92, 93, 94, which are benzo derivatives of cyclooctatrienone

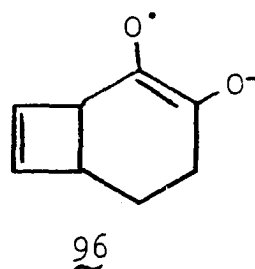
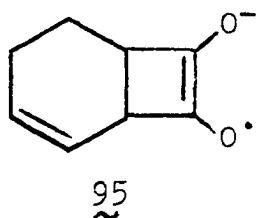


valence isomers, with basic DMSO again resulted in the production of the lawsone radical dianion. Presumably this radical is formed on oxidation in basic DMSO followed by decarbonylations via benzylic acid rearrangements or possibly through rearrangement and retro cycloaddition reactions.

In that the lawsone radical contains ten carbon atoms, it is quite surprising that it should arise from an eight

⁵R. L. Blankespoor, Unpublished results, Iowa State University, Ames, Iowa, 1972.

carbon precursor. It is, of course, possible that the observed radical is not the lawsone radical, but a radical whose esr spectrum is fortuitously identical. However, due to the stability of the lawsone radical and the great variety of means of generation, it must be considered as a serious possibility. Indeed, when probable precursors to semidiones 95 and 96 were allowed to react with basic DMSO under static



conditions the lawsone radical was again observed (Figure 8 and Figure 9). Also, since the synthetic routes in these two cases (Scheme 4 and Scheme 5) were quite different, it is highly unlikely that a common impurity could be a source of the radical.

If indeed the lawsone radical is produced from eight carbon sources, an explanation must be developed as to the source of the two added carbon atoms. If the chromyl chloride oxidation of cyclooctatetraene is considered (Scheme 6), the α -chlorotrienone 97 formed could react with basic DMSO via its bicyclic isomer 98 to give the semidione. Aromatization of the six-membered ring would result in

Figure 8. The first derivative esr spectrum of the radical obtained in DMSO from 8-chlorobicyclo[4.2.0]oct-2-en-7-one

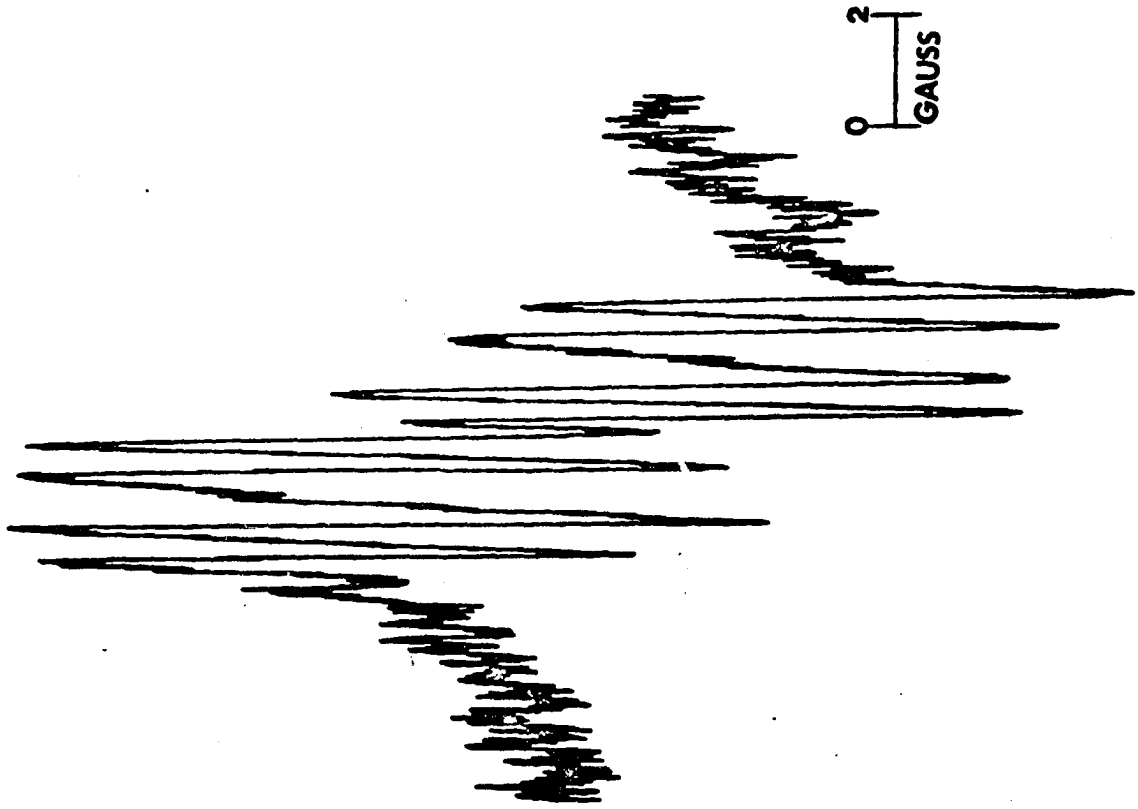
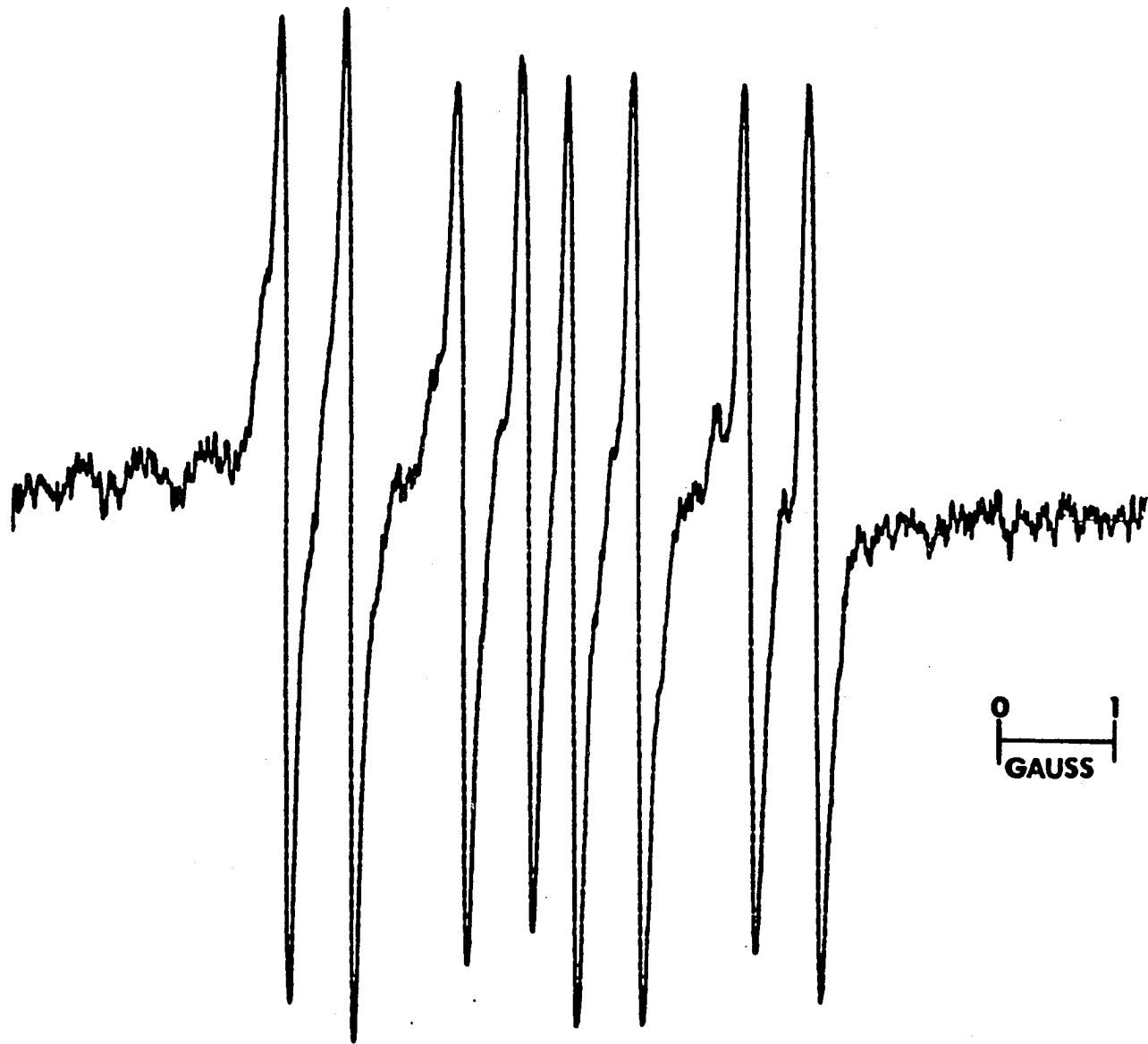
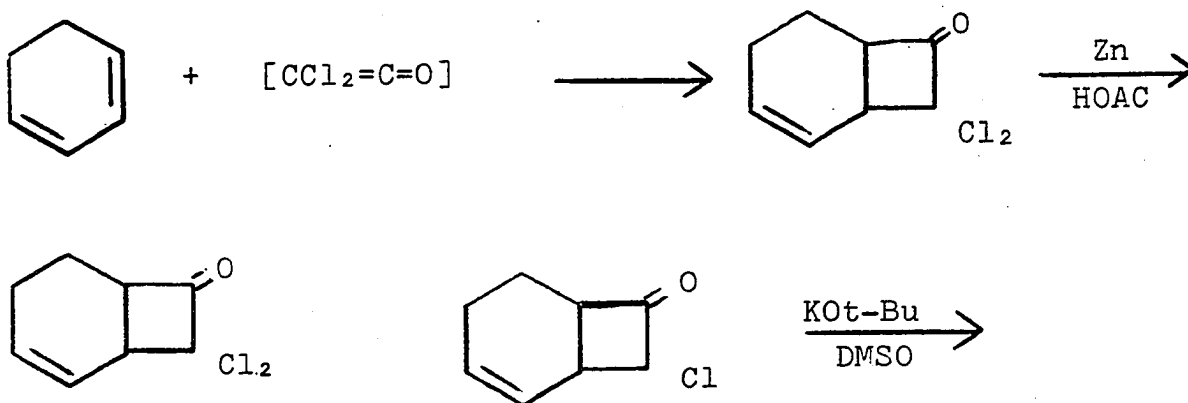


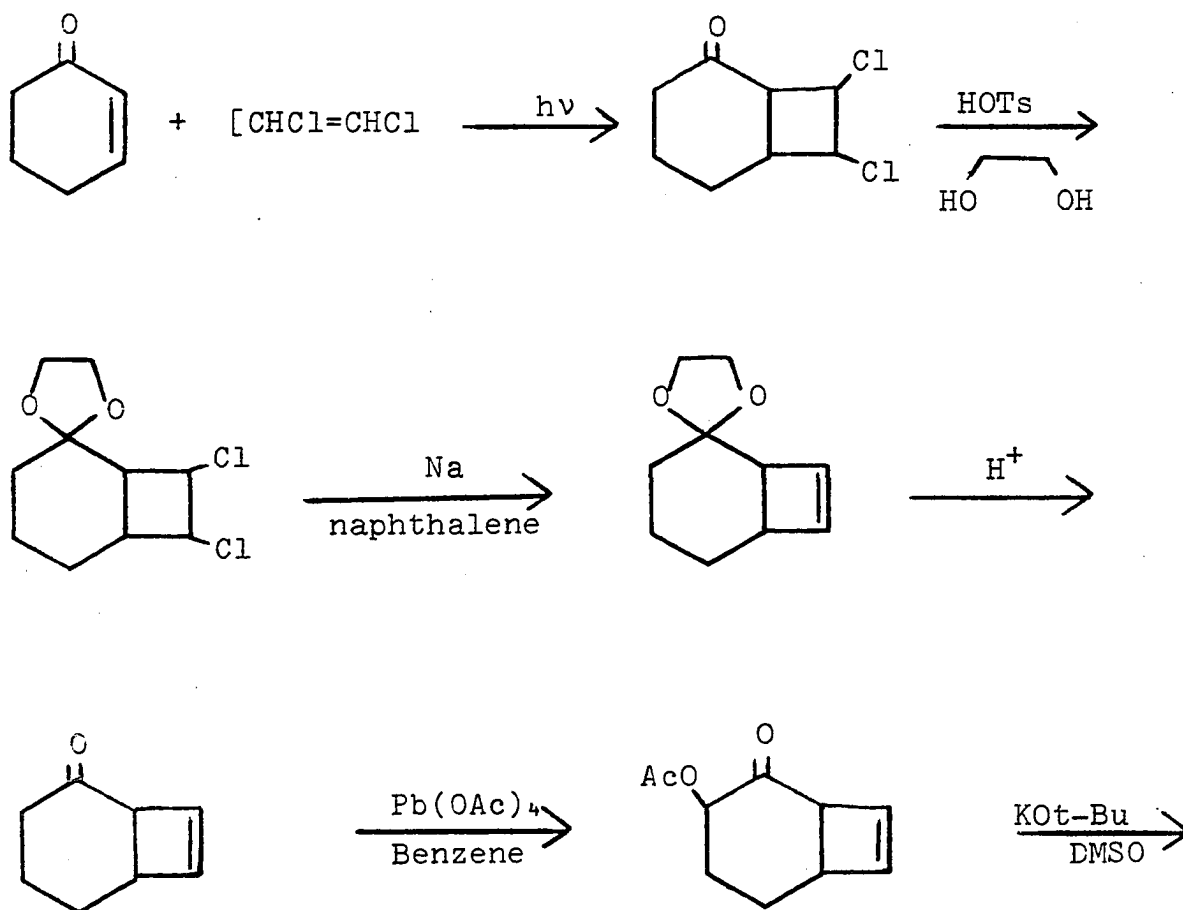
Figure 9. The first derivative esr spectrum of the radical obtained in DMSO from 3-acetoxycyclo[4.2.0]oct-7-en-2-one



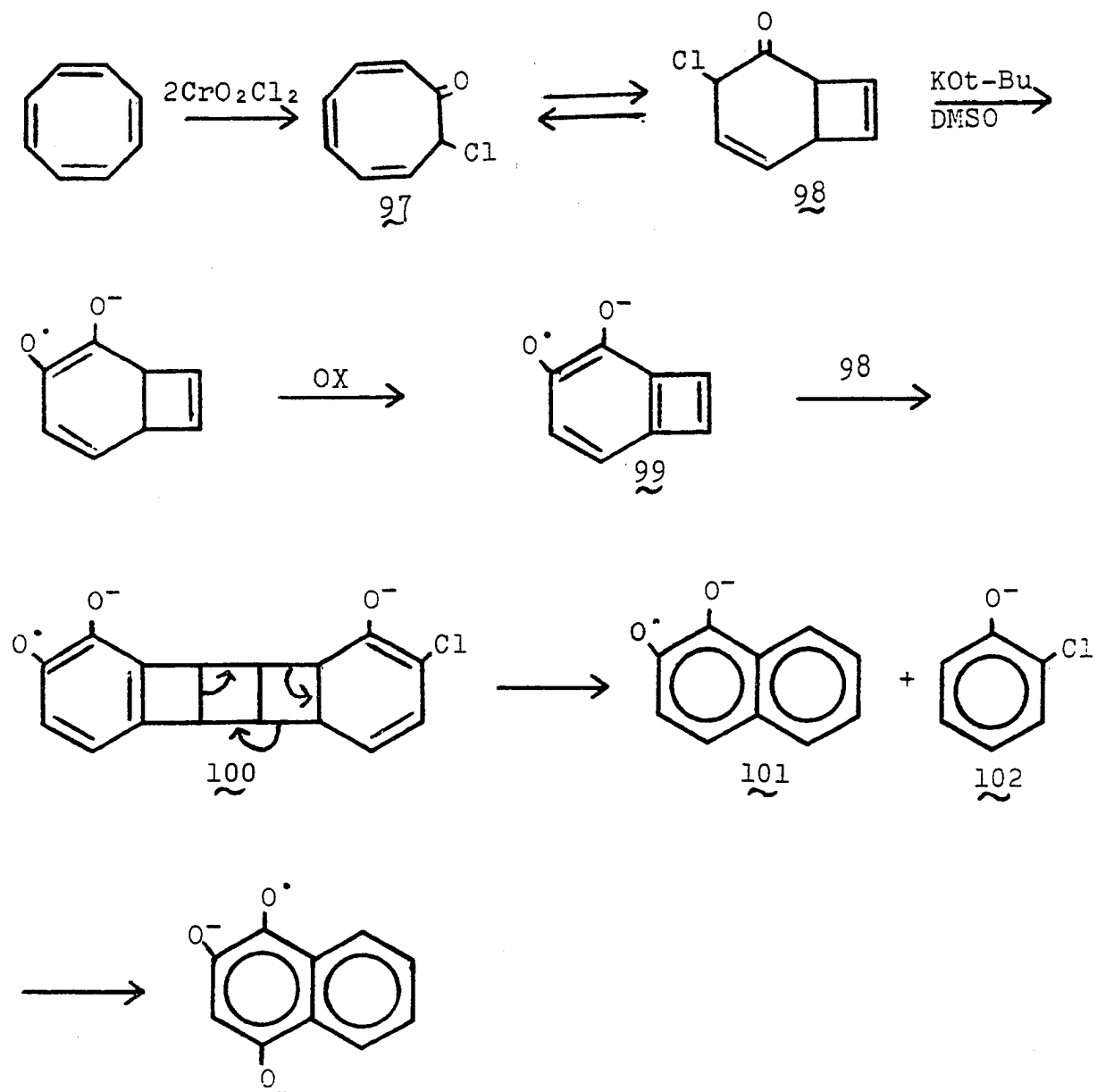
Scheme 4



Scheme 5

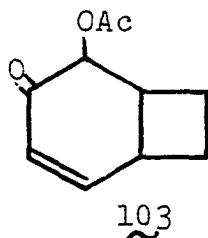


Scheme 6



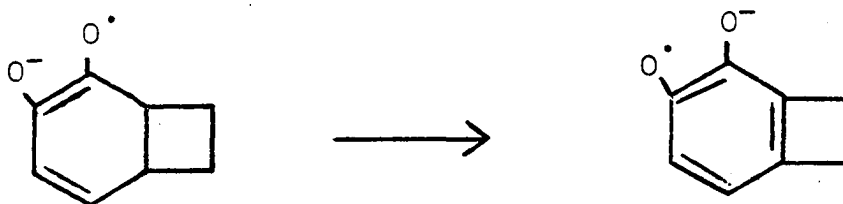
formation of a benzocyclobutadiene derivative 99. This cyclobutadiene could then undergo a cycloaddition reaction to form adduct 100, which subsequently breaks up into a six carbon fragment 102 and a ten carbon fragment 101, a known precursor to the lawsone radical dianion. A similar oxidation, addition, and fragmentation mechanism can be invoked for the other eight carbon precursors.

When 2-acetoxycyclo[4.2.0]oct-4-en-3-one 103 is

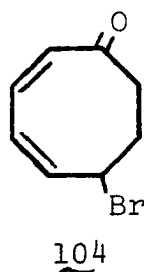


allowed to react with potassium t-butoxide in DMSO under flow conditions, no esr signal was seen. However, upon standing, especially in the presence of oxygen, a strong asymmetrical signal appeared, which obviously resulted from the presence of more than one paramagnetic species. The appearance of the spectrum changed with time, but at no time could the spectrum be interpreted as arising from one radical.

However, the lawsone radical could not be detected in the reaction mixture. This lack of detection is not surprising in this case as aromatization would not result in production of a cyclobutadiene derivative, and, thus, there would be no driving force for an addition reaction.

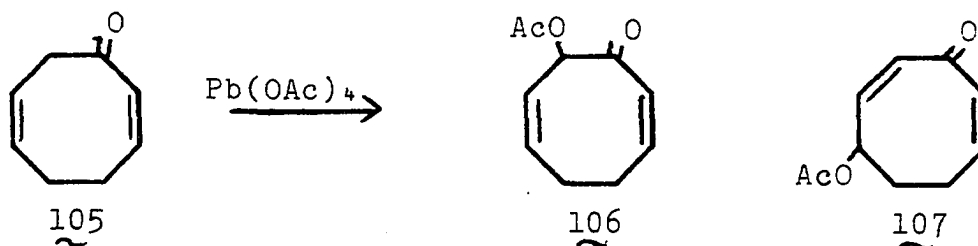


In the monocyclic series, when 6-bromocycloocta-2,4-dien-1-one 104,⁶ was allowed to react with basic DMSO, no



detectable radical was produced, even under flow conditions.

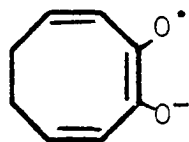
The reaction of cycloocta-2,6-dien-1-one 105 with lead tetraacetate in benzene gave a single acetoxy ketone. The



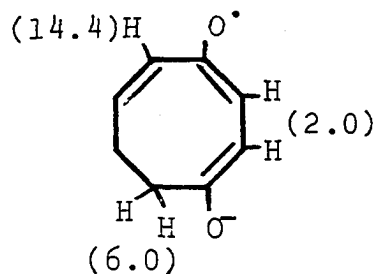
esr spectrum of this ketone under static conditions in basic

⁶Made concurrently by C. Tanger, Unpublished results, Iowa State University, Ames, Iowa, 1973.

DMSO consisted of a doublet of triplets of triplets [$a^H = 14.4$ G (1H); $a^H = 6.0$ G (2H); and $a^H = 2.0$ G (2H)] (Figure 10 and Figure 11), which is inconsistent for semidione 108 as it is symmetrical. Semidione 109 offers a possible explanation



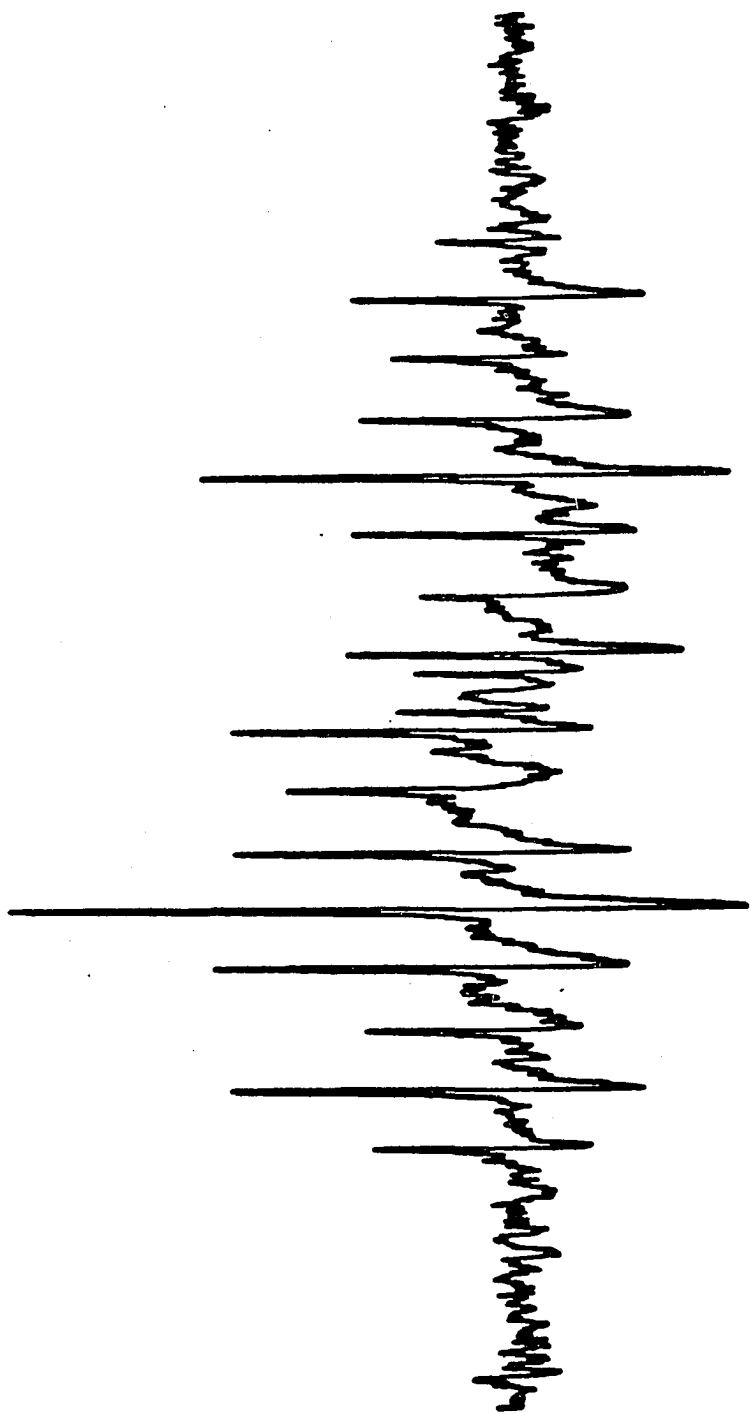
108



109

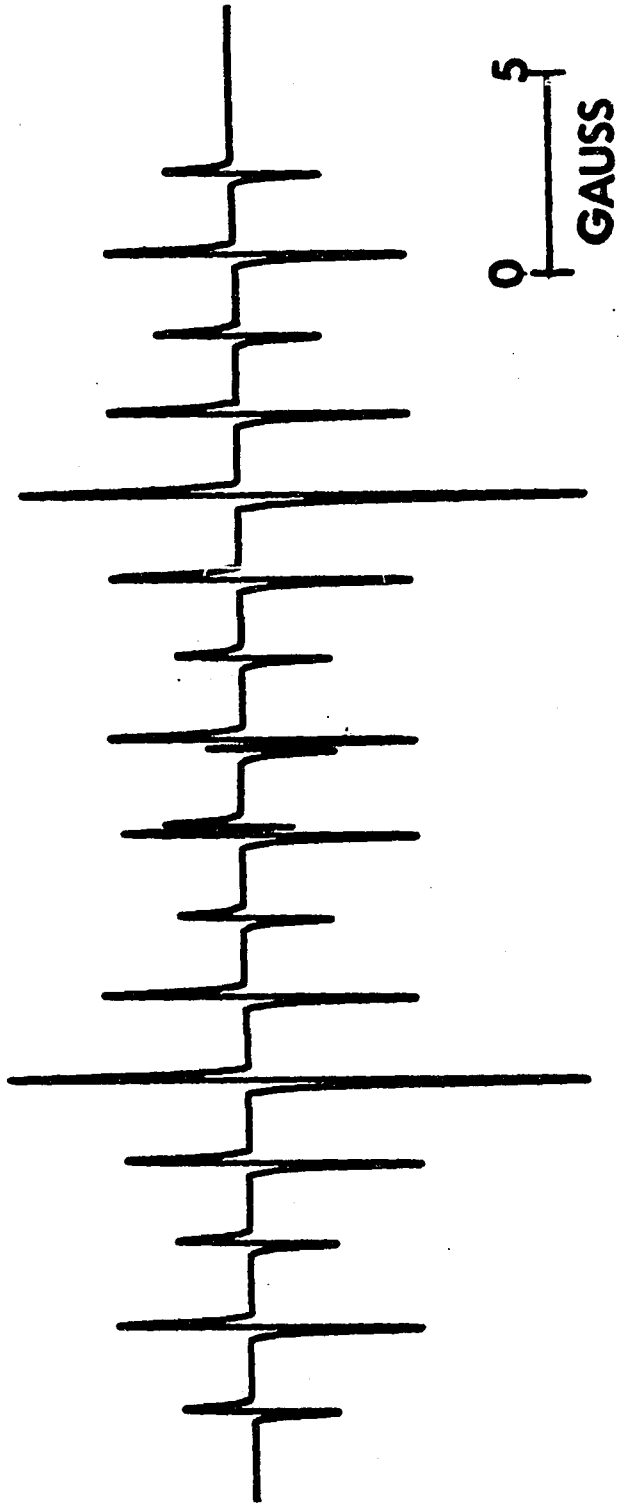
for the observed spectrum with the assignments as shown, a reversal of the 6.0 and 2.0 G assignments is possible. If the α -vinyl hydrogen atom is to have a hfsc of 14.4 G, which is quite large, it must assume a pseudo axial position; that is, the dihedral angle between the semidione π system and the sp^2 C-H single bond must be quite small. Since planarity of six consecutive carbon atoms, three double bonds, in an eight membered ring is sterically highly unfavorable and since the 1,4 semidione system must be planar for effective π delocalization, expulsion of the remaining double bond out of the plane is quite likely in the preferred conformation. This nonplanarity is supported by a Prentice-Hall model of semidione 109.

Figure 10. The first derivative esr spectrum of cycloocta-
2,5-diene-1,4-semidione (109) in DMSO

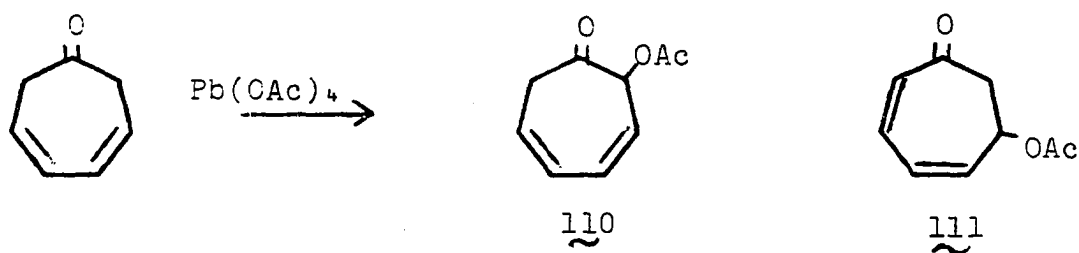


5
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GAUSS

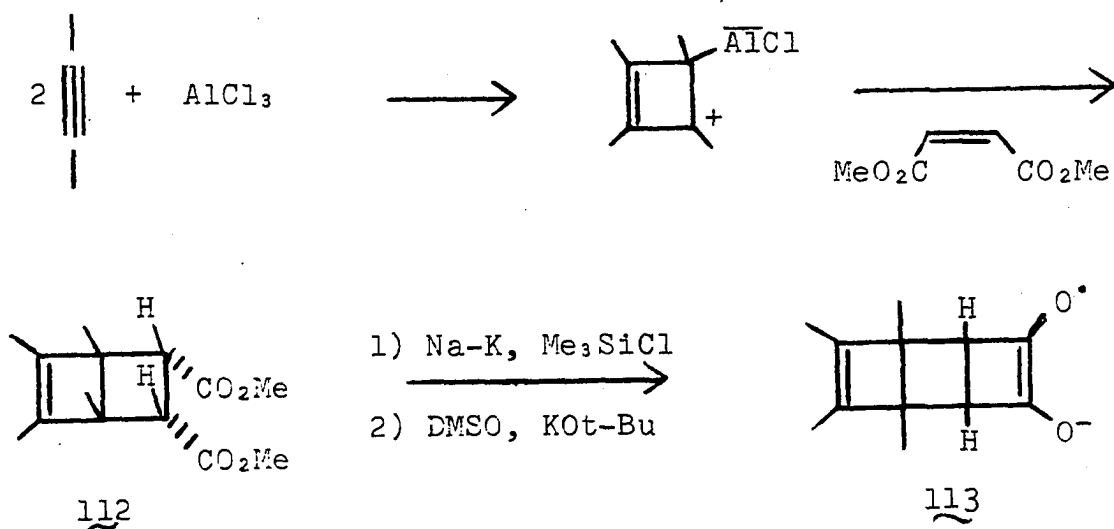
Figure 11. The calculated spectrum of cycloocta-2,5-diene-1,4-semidione (109) for Lorentzian line width 0.15 gauss and splitting constants from text performed by JEOLCO JNM-RA-1 spectrum accumulator



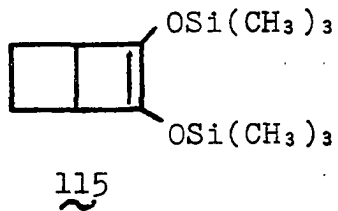
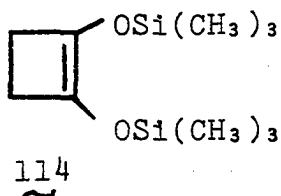
The origin of semidione 109 is quite possibly acetoxy ketone 107 which could arise from a double bond migration in the reaction of ketone 105 with lead tetraacetate. Indeed, a migration of this type was observed by Blankespoor (116) in the reaction of 3,5-cycloheptatrienone with lead tetraacetate at room temperature, in which the rearranged product 111 was obtained instead of the desired α -acetoxy ketone 110.



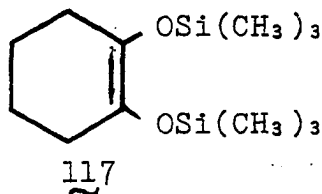
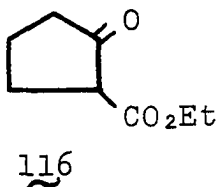
As a possible pathway to the tricyclic isomer 113 of cyclooctatriene semidione, the acyloin condensation on the diester 112, synthesized by Koster and co-workers (117) was



contemplated. Chances of success were considered mixed. Whereas, Rühlmann and co-workers achieved success in the synthesis of bis(trimethylsiloxy)cyclobutene 114 and other four membered ring derivatives (118), Bloomfield and co-workers (119) and Whittle (81) failed in their efforts to produce the corresponding bicyclohexyl derivative 115 from



cyclobutane dicarboxylate diester. Bloomfield obtained a low yield of the cyclopentanone 116 with no acyloin products isolated while Whittle's crude product generated cyclohexane



semidione upon treatment with basic DMSO in an esr cavity indicating 117 as an intermediate.

When the diester 112 was treated with Na-K alloy in refluxing xylene or at room temperature in diethyl ether utilizing trimethylchlorosilane as a trapping agent, a multi-component crude liquid was obtained (analysis by nmr and tlc).

When this crude product was allowed to react with basic DMSO under static conditions, an esr spectrum (Figure 12) containing signals from at least four distinct paramagnetic species, A, B, C, and D, (Table 2) was observed. Although there is some overlapping of peaks and the signal from radical C is quite weak, the individual spectra can be discerned. Upon standing, signals A, B, and C fade while D

Table 2. Hyperfine splitting constants of the esr signals in the spectrum seen in Figure 12

Signal	a^H
A	13.25 G (2H)
B	13.2 G (1H) 9.1 G (1H)
C	9.3 G (2H)
D	7.2 G (2H) 0.48 G (6H) 0.24 G (6H)

remains (Figure 13). There does not appear to be a growth of D at the expense of any of the other radicals, rather D is just more stable with time.

Purification of the initial crude reaction product proved difficult as the mixture was unstable to distillation, gas chromatography, and column chromatography on silica gel and alumina. Column chromatography on florisil did afford

Figure 12. The first derivative esr spectrum of the radicals obtained in DMSO from the crude product of the acyloin condensation of diester (112)

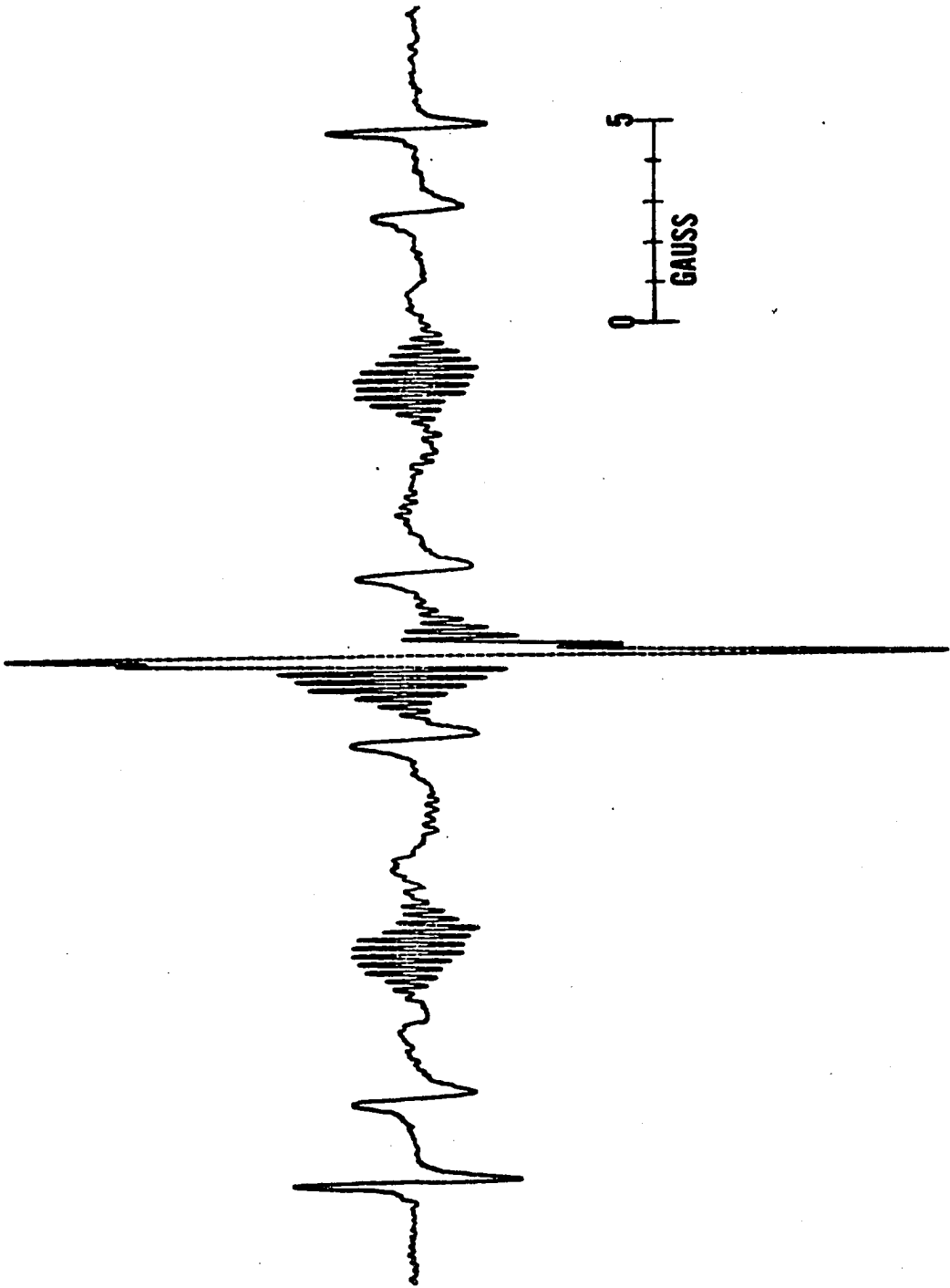
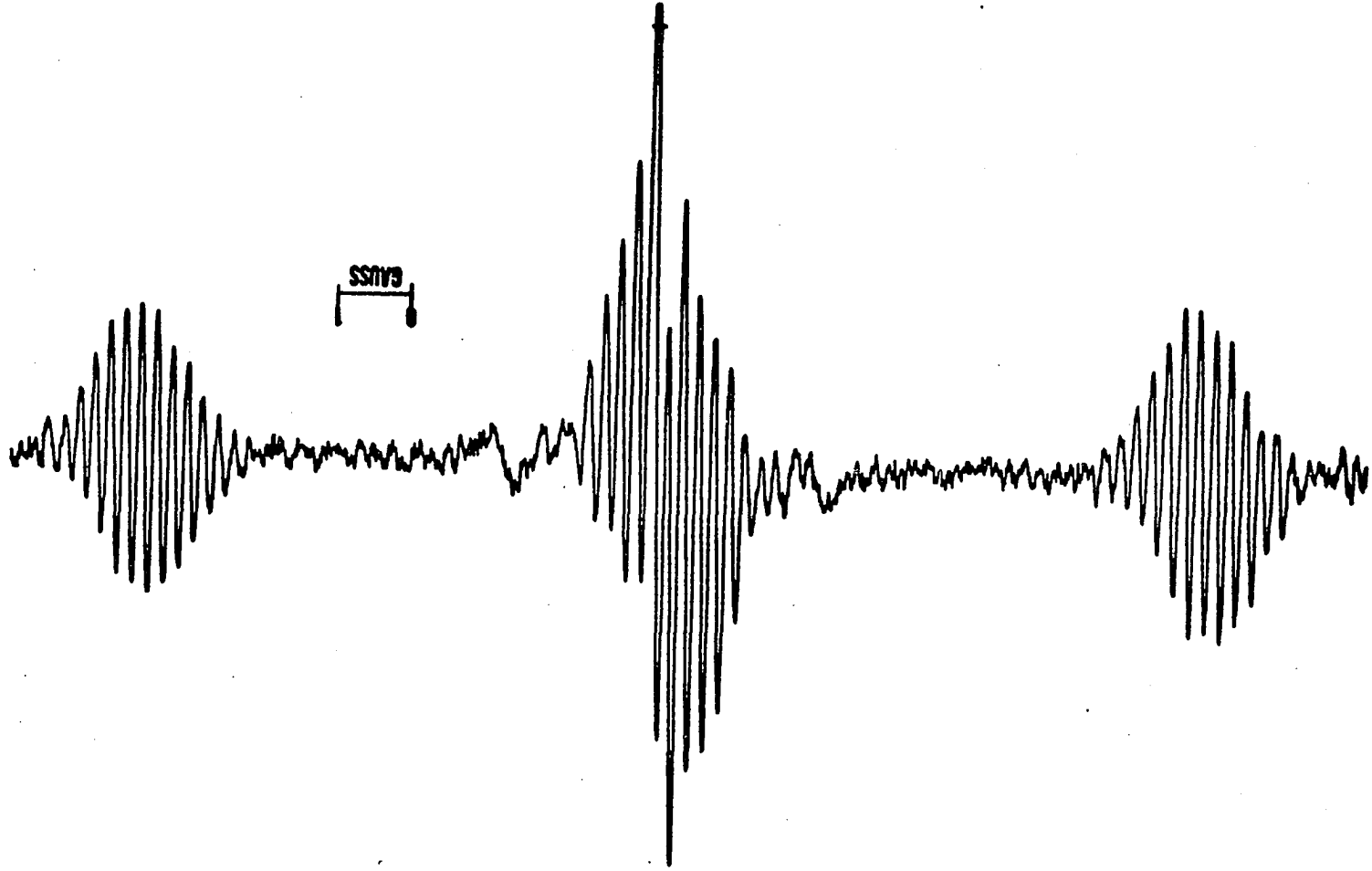
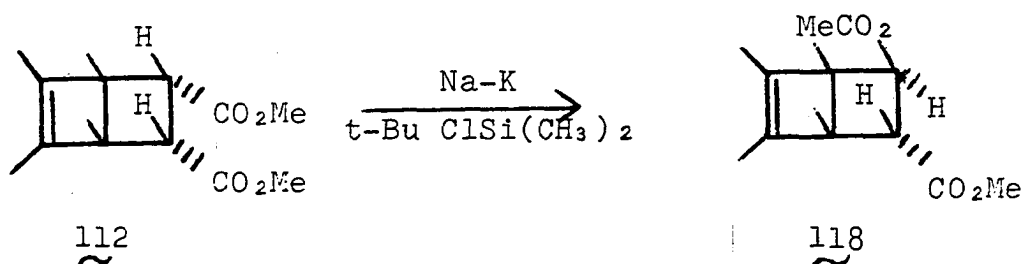


Figure 13. The first derivative esr spectrum of the radicals obtained in DMSO from the crude product of the acyloin condensation of diester (112) after standing



a fraction which yielded A, B, and C to the exclusion of D with basic DMSO (Figure 14). However, no D producing fraction was isolated indicating decomposition of the D precursor on Florisil.

An attempt was made to trap the acyloin products with *t*-butylchlorodimethylsilane instead of trimethylchlorosilane as the more sterically crowded silyl ethers have been shown to be more stable toward hydrolysis (120). However, the anions produced in the acyloin reaction were not trapped by the bulky reagent. Indeed, the major isolated product was the *trans*-diester 118.



When the acyloin condensation is run at -10° in diethyl ether and in the presence of trimethylchlorosilane, a multi-component mixture is again obtained. However, the reaction of this crude product with basic DMSO did not produce signal D, only A, B, and C (Figure 15).

Since a semidione is a possible intermediate in the acyloin condensation, the diester 112 was reduced by potassium in dimethoxyethane in the esr cavity. At 10° or above the

Figure 14. The first derivative esr spectrum of the radicals obtained in DMSO from the crude product of the acyloin condensation of diester (112) after chromatography on Florisil

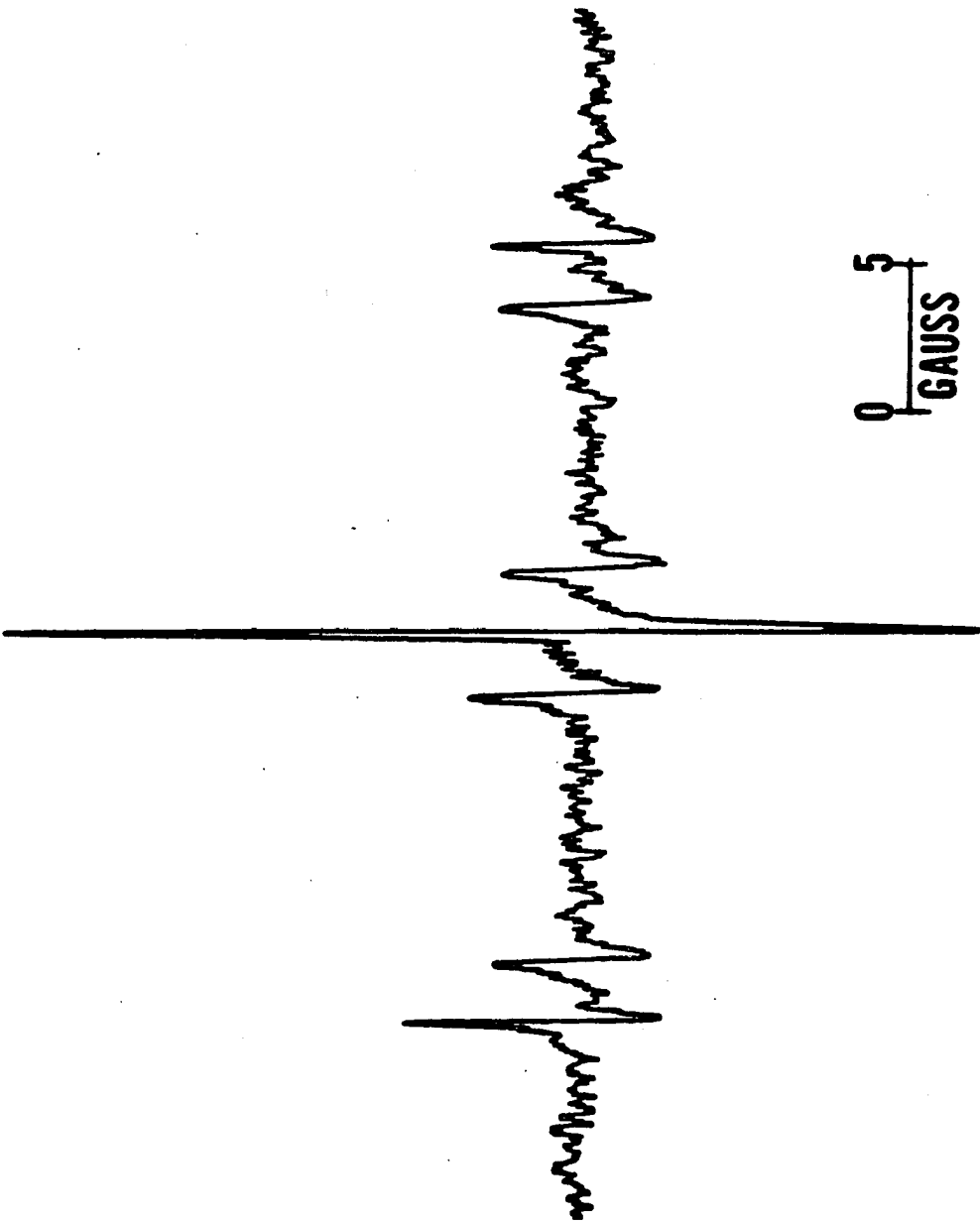
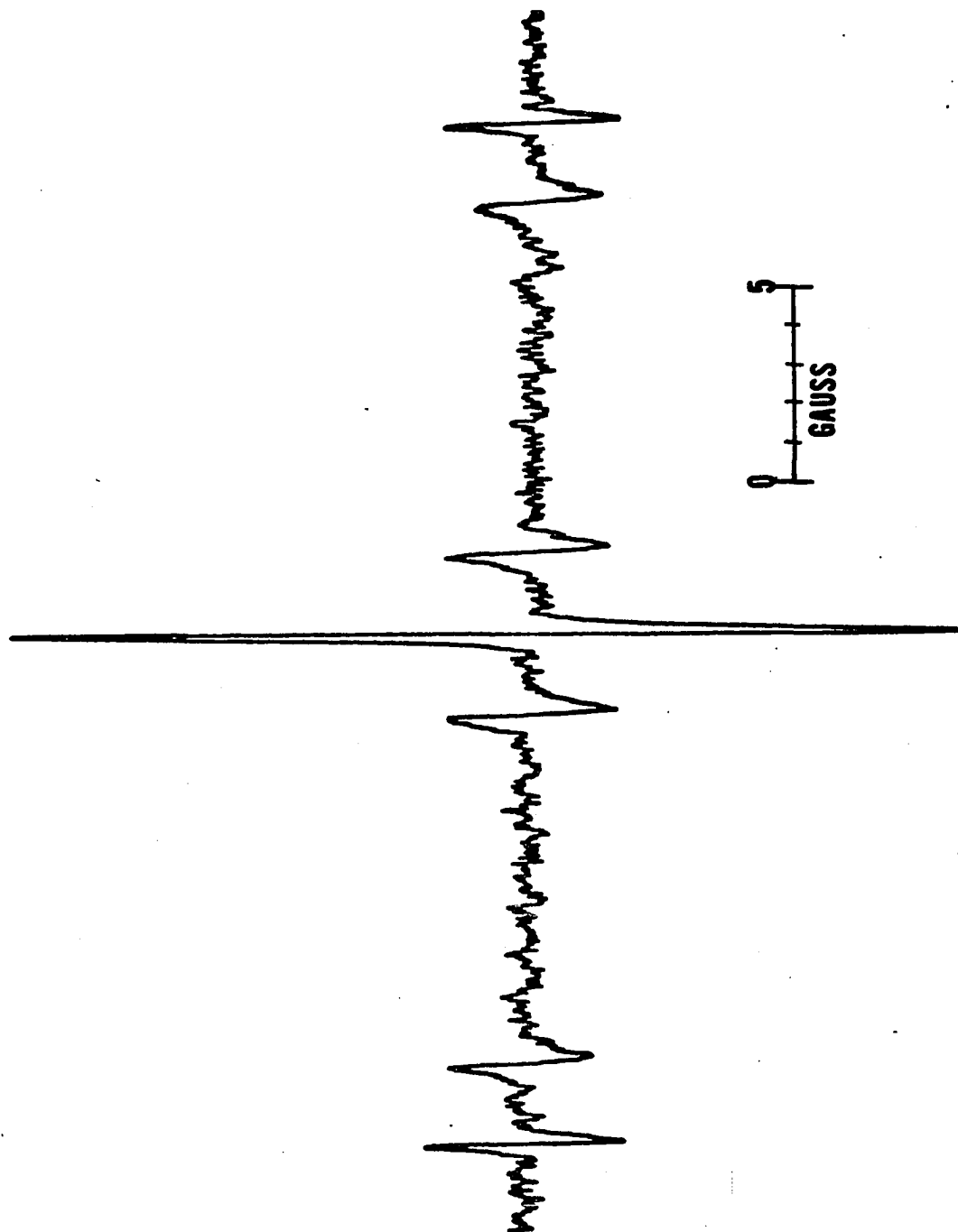


Figure 15. The first derivative esr spectrum of the radicals obtained in DMSO from the crude product of the acyloin condensation at -10°C in diethyl ether of diester (112)



only radical observed was D (Figures 16, 17, and 18). When the reduction is carried out at a temperature below 10°, only vague nondescript signals were obtained. Warming of this solution after reduction did not result in the production of D. Likewise, cooling of the solution in which D was produced resulted in a decrease in intensity of D without the production of any new observable radicals. At no time could A, B, or C be observed.

Thus, from the above mentioned results, A, B, and C must be treated as a unit as none of these signals has been observed individually but only in conjunction with the other two. Signal D, however, is separate and apart, and at no time was an interconversion between D and the others observed. It must, therefore, be concluded that the generation of the precursor to radical D must take place by rearrangement during the acyloin rearrangement prior to semidione formation as the semidiones do not interconvert.

Structural assignments for the observed radicals must be in the realm of speculation as an unambiguous route to their generation was not attained. However, tentative assignments can be made based on similar model systems. Signal A can be readily attributed to the expected unrearranged semidione 119 as substituted cyclobutane semidiones exhibit

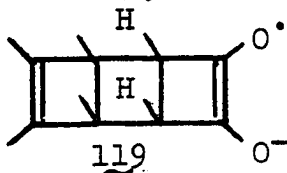


Figure 16. The first derivative esr spectrum of the radical obtained from the diester (112) upon reduction by potassium in dimethoxy ethane in the esr cavity

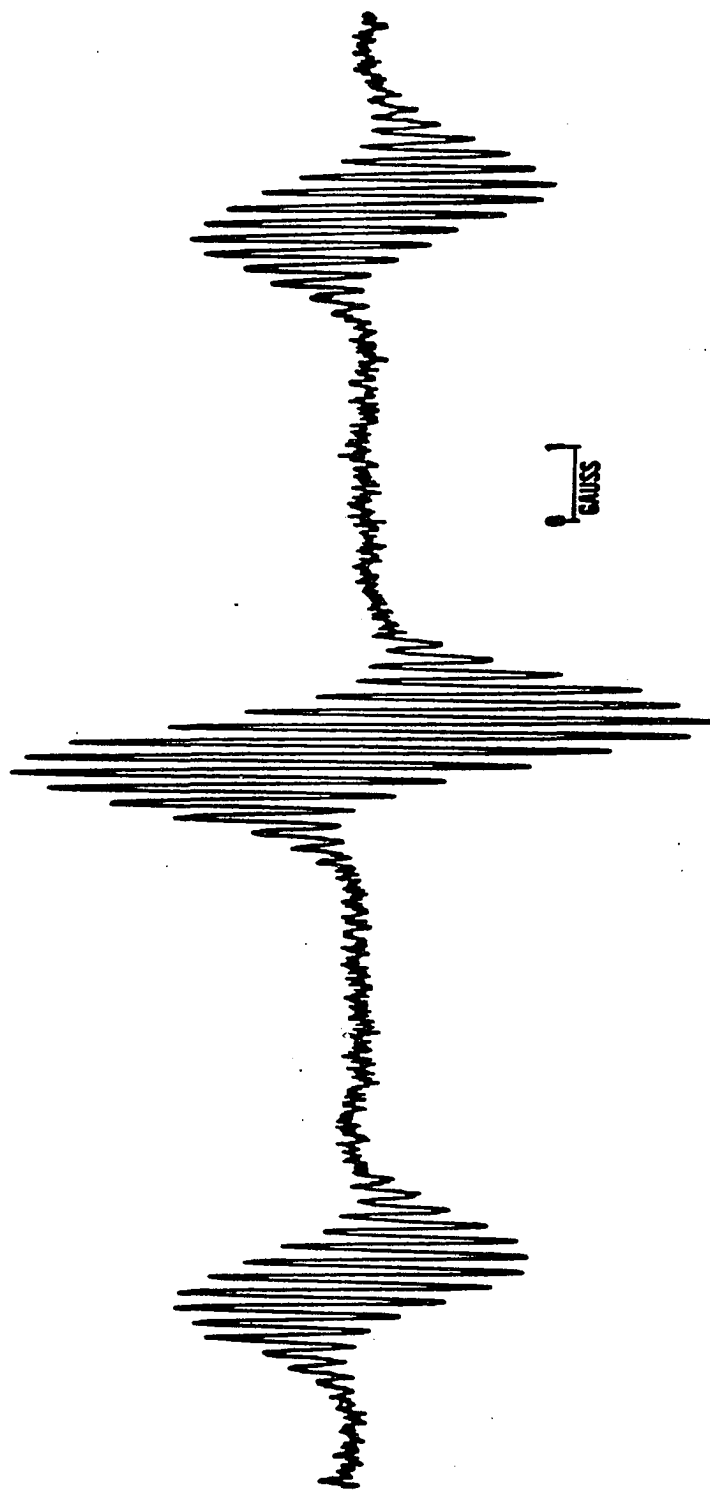


Figure 17. The calculated spectrum of the radical obtained from the potassium reduction of diester (112) in dimethoxy ethane for Lorentzian line width 0.12 gauss and splitting constants from text performed by JEOLCO JNM-RA-1 spectrum accumulator

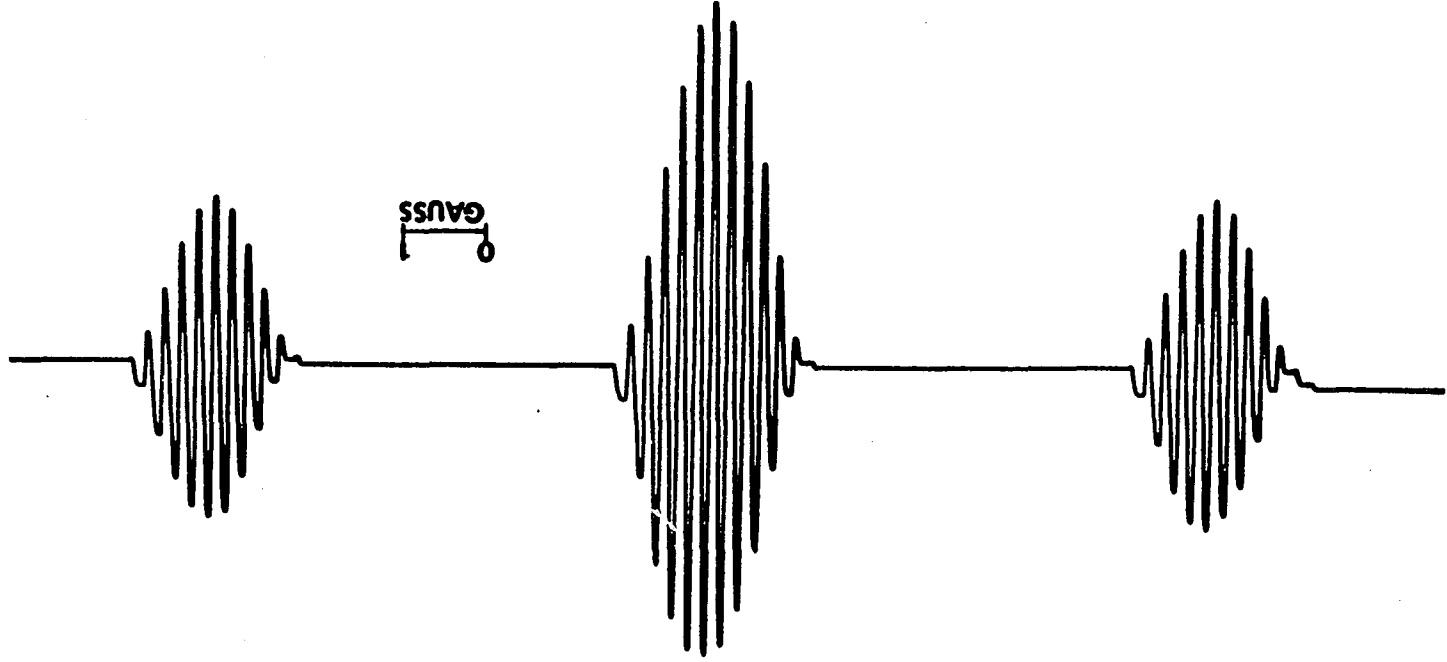
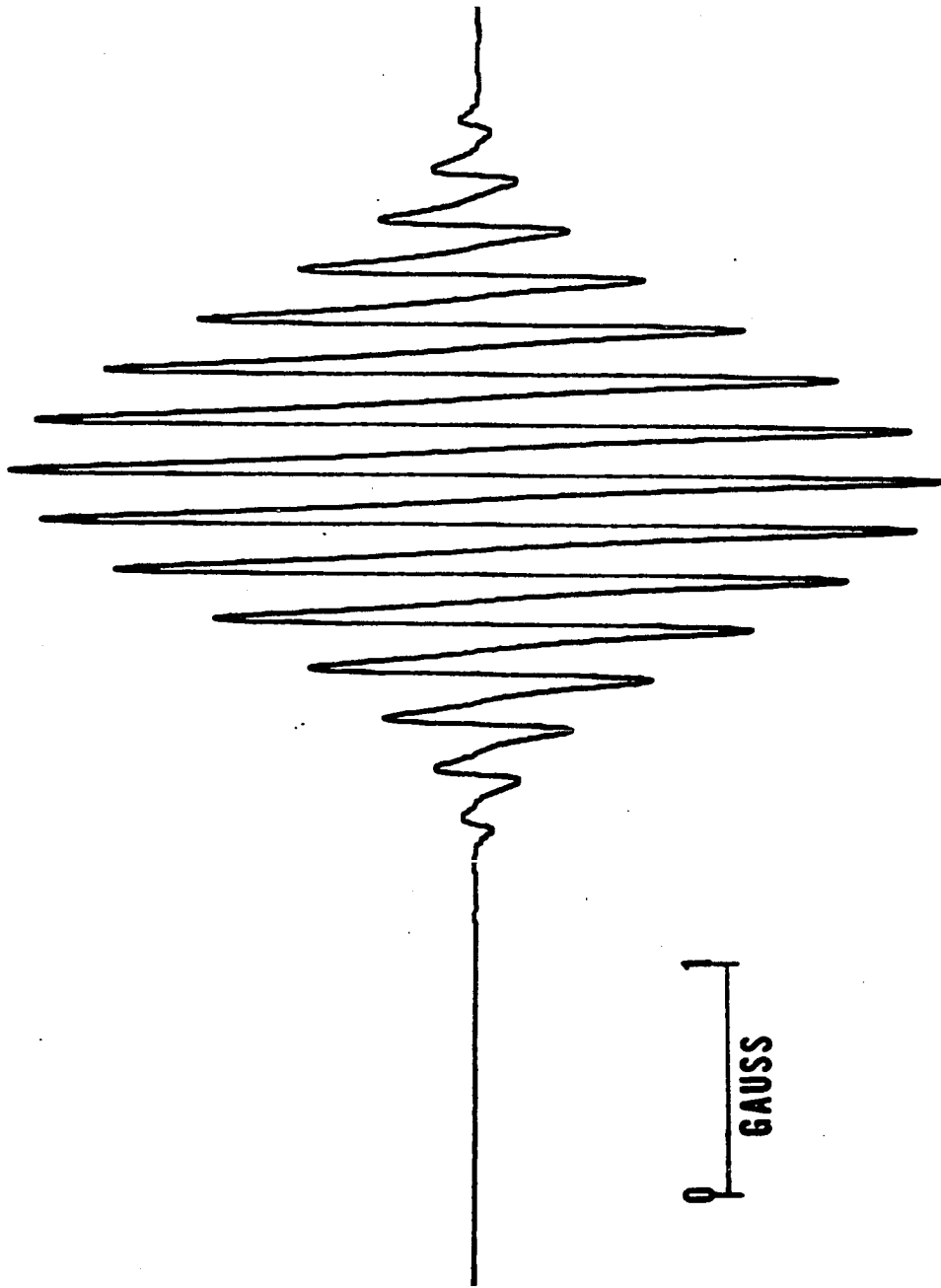
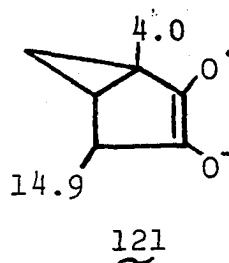
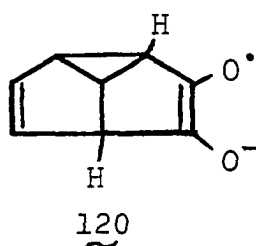


Figure 18. An expansion of one section of the calculated spectrum of the radical obtained from the potassium reduction of the diester (112) in dimethoxyethane for Lorentzian line width 0.12 gauss and splitting constants from text performed by JEOLCO JNM-RA-1 spectrum accumulator

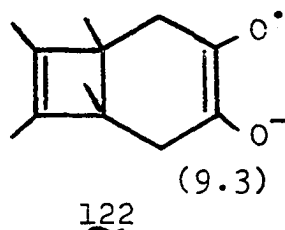


splitting for the α -hydrogen atoms in the 13 gauss range. Assignment of a structure to signal B is much more arbitrary. An asymmetrical semidione is required because of the magnetic nonequivalence of the two observed hydrogens. Also, the large splitting constant (13.2 G) implies a pseudo axial conformation of one of the hydrogen atoms. The semibullvalene semidione 120 is a possibility as the axial hydrogen in



bicyclo[3.1.0]hexane semidione 121 has a hfsc of 14.9 G (81).

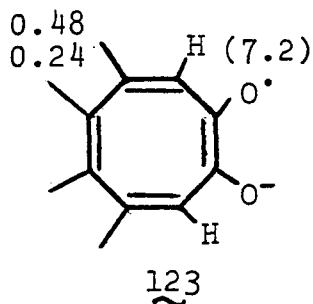
The weak signal C, although it appears to be a triplet, is most likely a quintet arising from semidione 122 in a



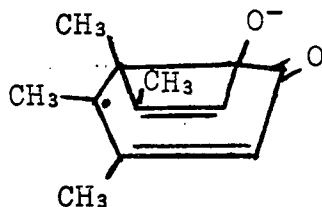
process similar to that observed by Whittle (81) in the acyloin condensation of cyclobutane dicarboxylate diester, in which cyclohexane semidione ($4H$, $a^H = 9.9$ G) was generated.

Signal D is the most interesting in that it has the longest lifetime of these radicals, it can be seen

independently of the other radicals, and that every hydrogen atom and every methyl group is observed in the spectrum. The most intriguing and appealing assignment of D is to the monocyclic semidione 123, 4,5,6,7-tetramethylcycloocta-3,5,7-triene-1,2-semidione. Indeed, this radical anion best fits

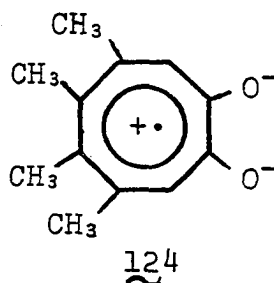


the data as it possesses three sets of equivalent hydrogen atoms and yet is not a substituted cyclobutane semidione derivative in which a splitting of about 13 G would be expected for the α hydrogens. Also, a bis-homohyperconjugative mechanism can be postulated to account for the splitting of the γ -methyl groups. In that the tub conformation

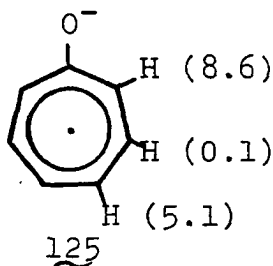


would be preferred for this radical anion, this through space interaction would indeed be quite favorable due to the proximity of the atoms involved. A definite assignment of the

0.48 G and 0.24 G splittings cannot be made. A planar conformation, such as 124, for this radical anion is extremely

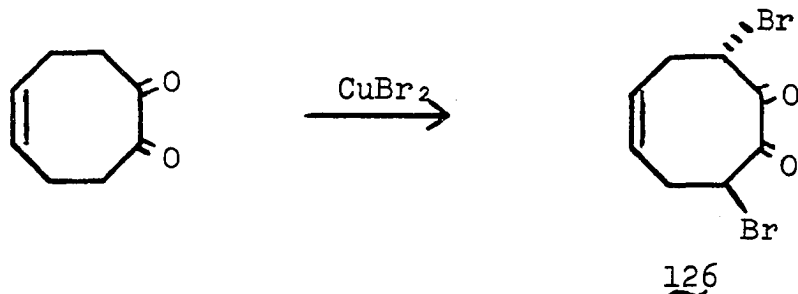


unlikely because the resonance energy gained by π -delocalization throughout the system must be great enough to overcome not only the steric strain encountered by a planar eight membered ring of sp^2 hybridized carbon atoms but also the severe eclipsing of the four methyl groups necessitated by planarity. Also, the hfsc's of two of the methyl groups should be larger in analogy to the tropone ketyl (110), which is planar and possesses the same number of electrons

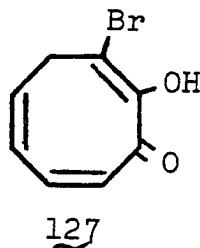


in the ring as 124. Indeed, INDO calculations for the tub conformation predict that a_{α}^H is large and a_{β}^H and a_{γ}^H are small (121).

The final system to be considered is 3,8-dibromocyclo-oct-5-ene-1,2-dione 126, which was synthesized by Kowar (80)



by the treatment of the dione 45 with cupric bromide. Attempts at dehydrobromination with base were not fruitful, with the lone exception of heating with hexamethylphosphoric triamide (HMPA), in which the mono-bromo enol 127 was produced.



When the dibromide 126 was allowed to react with KOt-Bu and DMSO under flow conditions, three distinct signals, X, Y, and Z, were observed in the spectrum (Table 3) (Figure 19). All three signals were short-lived as stoppage of the flow resulted in cessation of the signals. Also, the relative concentrations of the radicals causing X, Y, and Z did not change upon varying the ratio of KOt-Bu to dibromide from 3.5:1 to 10:1.

Figure 19. The first derivative esr spectrum obtained
from 3,8-dibromocyclooct-5-ene-1,2-dione
(126) in DMSO

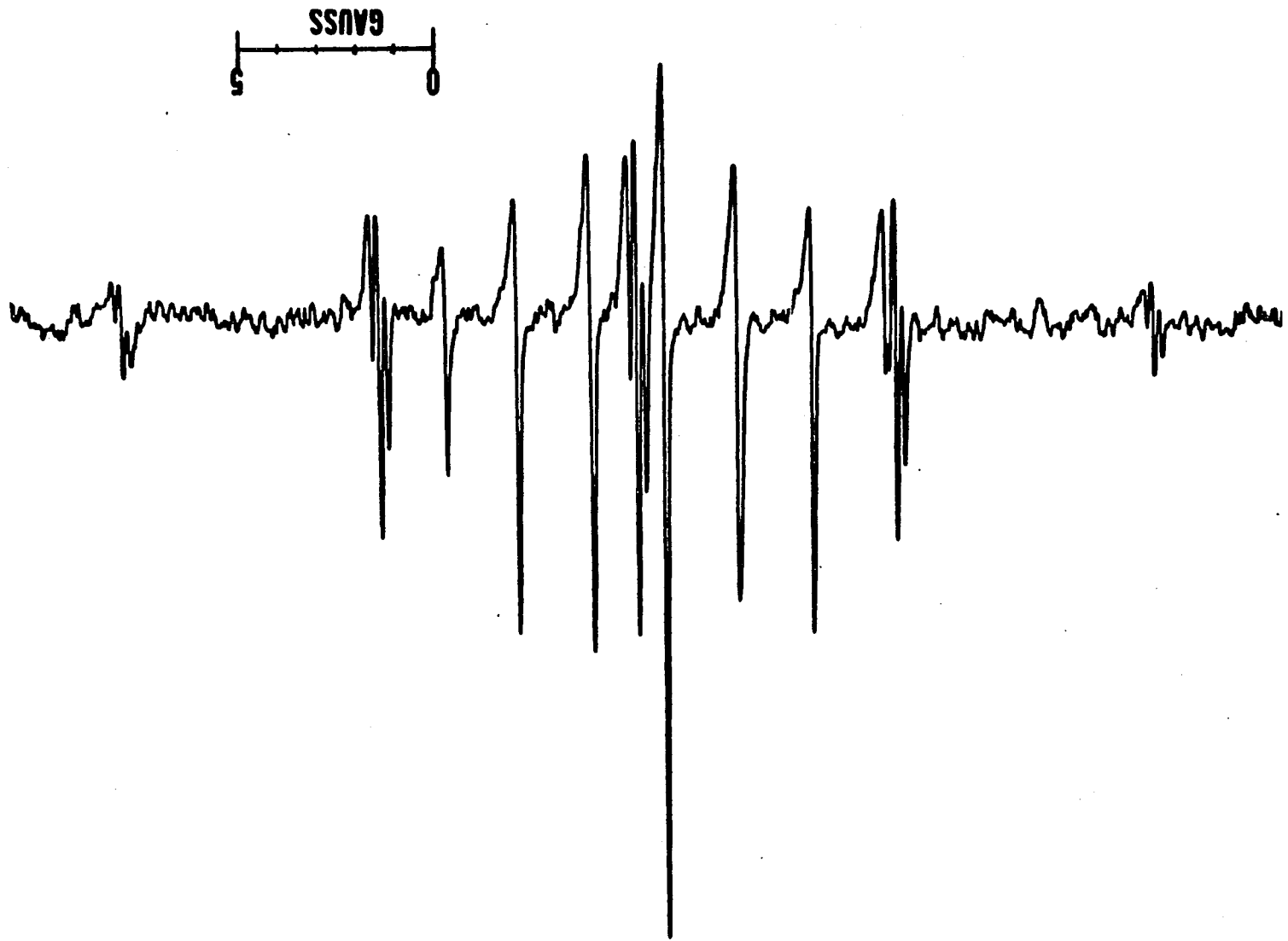
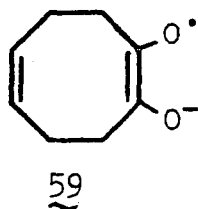


Table 3. Hyperfine splitting constants of the esr signals observed when dibromide 126 was reacted with KOt-Bu and DMSO under flow conditions

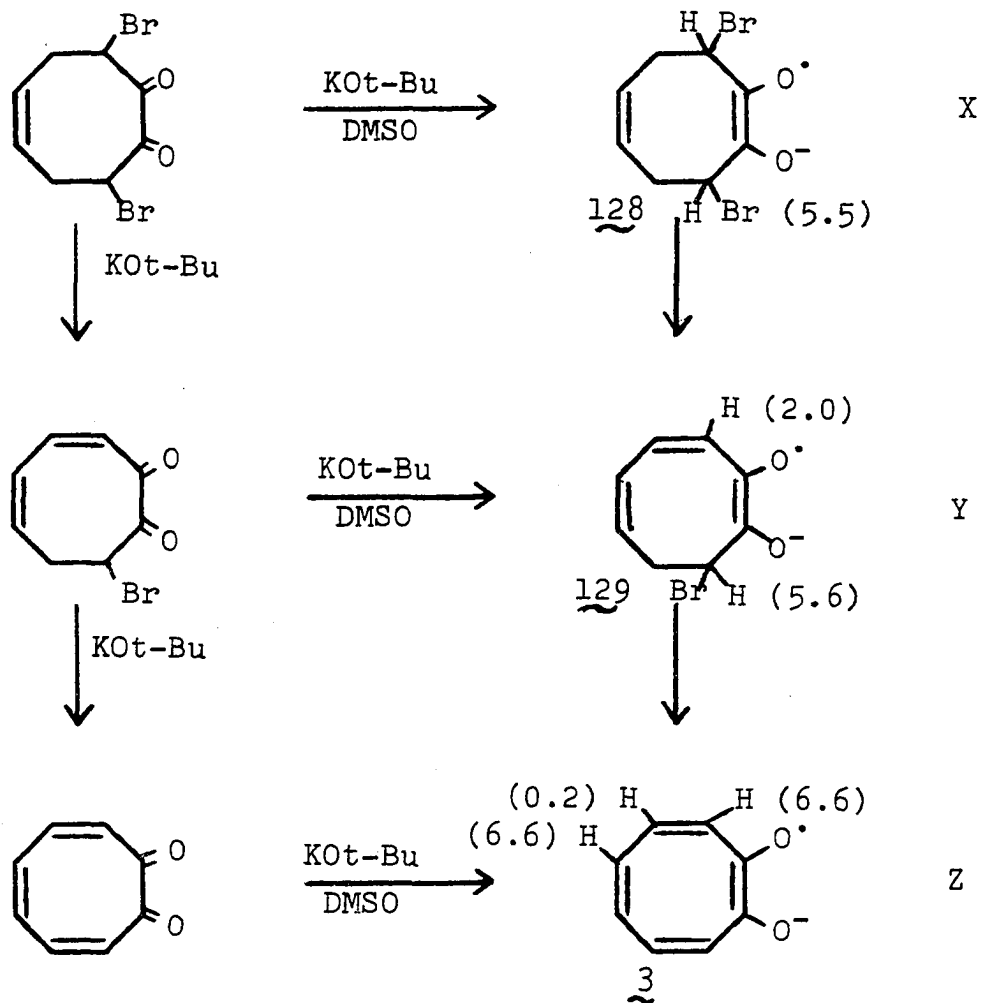
Signal	a^H
X	5.5 G (2H)
Y	5.6 G (1H) 2.0 G (1H)
Z	6.6 G (4H) 0.2 G (2H)

A postulation as to the origin and the assignments for X, Y, and Z can be found in Scheme 7. If it is remembered that the esr spectrum of 5-cyclooctene-1,2-semidione 59 exhibits splitting from four hydrogen atoms ($a^H = 4.5$ G),



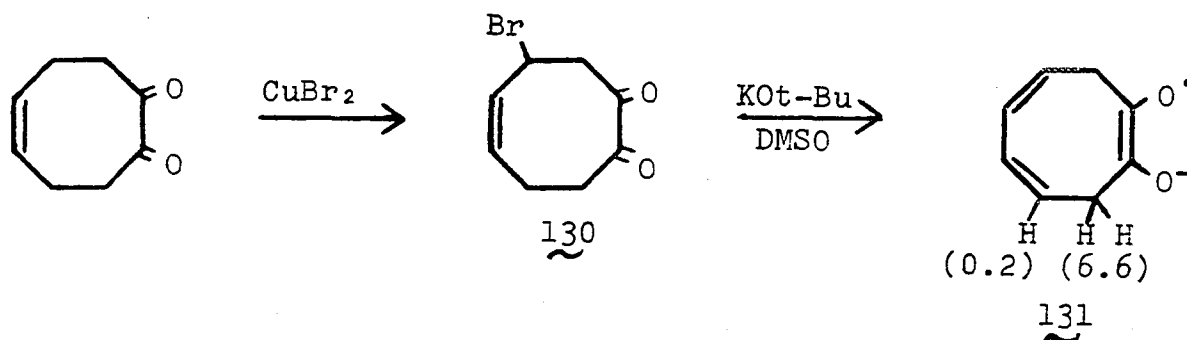
an assignment of X to the parent semidione 128 can be readily made. A monodehydrobromination would change the environment of one α -hydrogen atom while leaving the other α -hydrogen essentially unchanged (Y). The next logical step would be an additional monobromination step from which from the cyclooctatriene semidione 3 could be generated. If signal Z is to be ascribed to 3, it is necessary that the splitting by the

Scheme 7



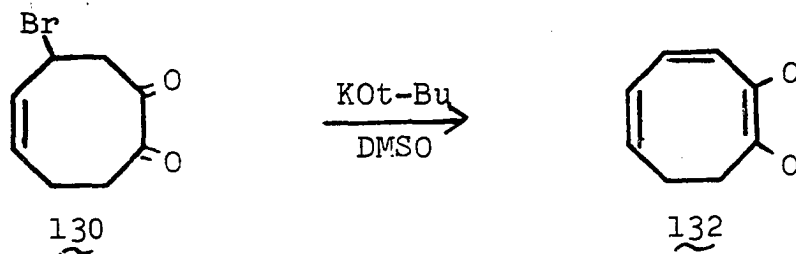
α and γ hydrogen atoms be large (analogous to the tropone ketyl) and fortuitously equivalent. The large γ splittings would necessitate spin delocalization through the π system for which planarity would be required. Thus, cyclooctatriene semidione derivatives would have been observed in both tub and

planar conformations depending upon the steric interactions of the substituents. Since this result is both surprising and noteworthy, alternate assignments for Z were sought. Indeed, the equivalence of four hydrogen atoms ($a^H = 6.6$ G) suggests two methylene groups alpha to the semidione functionally. Since the parent diketone 126 has a bromine atom in each α -position, it is unlikely that such a radical could be formed from it. However, if the chemical origin of 126 is traced, the monobromide 130 looms as a possible

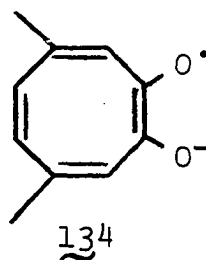
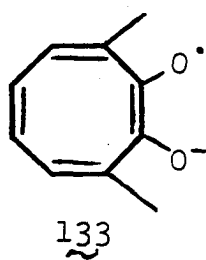


impurity. Treatment of 130 with basic DMSO could indeed generate a semidione 131 with 4 α -hydrogens ($a^H = 6.6$ G) and 2 β -hydrogens ($a^H = 0.2$ G) as likely assignments. However, this monobromide could not be detected by tlc, nmr, or high resolution mass spectral analysis. Also, since non-conjugated semidiones generally have a longer lifetime than nonaromatic α, β -unsaturated semidiones, 131 would be expected to possess increased stability and a longer lifetime compared to X and Y, which is not the case. Since the most acidic

protons in 130 are alpha to the carbonyl group, semidione 132



should also be seen, but is not. Thus, it is unlikely that any 130 is present as an impurity, but this possibility must be considered until substituted semidiones such as 133 and 134 have been observed.



EXPERIMENTAL

Reagents

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

Preparation of Semidiones

The semidiones observed under static conditions were prepared in DMSO solution in the standard apparatus by methods previously described (122). The semidiones observed under flow conditions were prepared in the manner and apparatus as described by Schmitt (6).

Recording and Simulation of ESR Spectra

The esr spectra were recorded on a Varian E-3 spectrometer (4 inch magnet and 100 KHz field modulation). The esr spectra were simulated on a JNM-RA-1 spectrum accumulator (Japan Electron Optics Company) utilizing a program to fit variable Lorentzian line width to a stick diagram of the spectrum.

Characterization of Compounds

Pmr spectra were recorded either on a Varian A-60 spectrometer or a Perkin-Elmer/Hitachi R-20B spectrometer. Infrared spectra were recorded on a Perkin-Elmer Model 21

or a Beckman Model IR-18 Infrared Spectrometer. Mass spectra were obtained either on an Atlas CH4 spectrometer or an AEI-MS-902 spectrometer. Melting and boiling points were uncorrected.

Preparation of Compounds

General procedure for preparing acetoxy ketones

A mixture of the ketone, 1.1 equivalents of lead tetraacetate, and dry benzene (100 mls/0.05 moles of ketone) was heated to reflux with stirring for 2-3 days as described by Ellis (123). After cooling, the benzene solution was washed with water, sat'd NaHCO₃, and sat'd NaCl and dried (MgSO₄). Removal of the benzene under vacuum gave the crude acetoxy ketone.

General procedure for the recovery of an organic product from a DMSO solution

The DMSO solution containing the organic compound was dissolved in twice its volume of ether. This ethereal solution was washed first with ice water, then four times with water, and finally with sat'd NaCl. The volume of each wash was approximately equal to volume of the ethereal solution. The resultant solution was dried (MgSO₄), and the ether was removed under reduced pressure leaving the crude product.

Lead tetraacetate

The title compound was synthesized from lead dioxide by the method of Vogel (124) and recrystallized from acetic acid.

8-Hydroxycyclooct-4-en-1-one

This α -hydroxyl ketone was made in a manner as described by Kowar (80). The monoepoxide of 1,5-cyclooctadiene, produced by the oxidation of the diolefin with *m*-chloroperbenzoic acid, was oxidized by boron trifluoride-dimethyl sulfoxide solution to give the title compound: bp 77-79° (0.8 mm) [Lit. (77) 78-79° (0.5 mm)].

3,8-Dibromocyclooctene

The dibromide was prepared by the low temperature addition of one equivalent of bromine to 1,3-cyclooctadiene in methylene chloride as performed by Cope and Estes (125).

4-Bromocyclooct-2-en-1-one

To a solution of 5.4 g AgClO_4 (0.02 mole) in 40 ml of DMSO was added in one portion 4.1 g crude 3,8-dibromocyclooctene (0.02 mole). A light yellow precipitate (AgBr) formed immediately upon addition. The reaction mixture was allowed to stir for 5 hrs at room temperature at which time the solution had turned brown. The precipitate was filtered with the aid of celite and washed (2 x 10 ml ether). The product was recovered from the DMSO solution as

per the general procedure giving a brown oil. Purification by column chromatography (9:1; hexane:ethyl acetate) on silica gel gave pure ketone: ir (neat) 1685 (C=O) and 1650 cm^{-1} (C=C); pmr (CDCl_3) δ 6.25 and 5.62 (AMX, 2H, $J_{AM} = 12.3$ Hz, $J_{AX} = 5.0$ Hz, and $J_{MX} = 2.0$ Hz), 5.18-4.81 (m, 1H), and 3.0-1.5 (m, 8H).

MS Calcd. for $\text{C}_8\text{H}_{11}^7\text{BrO}$: 201.9994.

Found: 201.9984.

Bicyclo[4.2.0]octan-2-one

As indicated by Owsley and Bloomfield (126), 2 g of cyclohex-2-en-1-one (obtained from J. Dodd) was dissolved in 200 ml of dichloromethane. The solution was first degassed with N_2 and saturated with ethylene. The solution was irradiated (Hanovia 450 W lamp and corex filter) for 5 hrs until it appeared that most of the starting material had disappeared (nmr analysis). During the irradiation, the dichloromethane solution was cooled in a Dry Ice-ethanol bath in a quartz Dewar, and ethylene was slowly bubbled through. The crude photolysis mixture was distilled, and the cyclohexenone remaining in the distillate was removed by chromatography on silica gel (9:1; hexane:ether) giving pure bicyclo[4.2.0]octan-2-one, whose pmr spectrum agrees with that determined by House and Cronin (127): (CDCl_3) δ 3.2-2.5 (m, 2H) and 2.5-1.2 (m, 10 H).

3-Acetoxybicyclo[4.2.0]octan-2-one

Bicyclo[4.2.0]octan-2-one was allowed to react with $\text{Pb}(\text{OAc})_4$ as described in the general procedure for 3 days to give a yellow liquid. Purification by glpc (10% SE30 column) gave a mixture of the endo and exo acetates: ir (neat) 1750 (ester C=O), 1725 (C=O), and 1235 cm^{-1} (C-O-C); pmr (CCl_4) δ 5.3-4.8 (m, 1H), 3.1-1.3 (m, 13H, acetate singlets at 2.0 and 1.9).

MS Calcd. for $\text{C}_{10}\text{H}_{12}\text{O}_3$: 180.0786.

Found: 180.0796.

Dichlorovinylene carbonate

This compound was prepared by the method of Holland (122): bp 66-72/35 mm [Lit. (128) 65-70/35 mm].

2,6-Dichloro-3,5-dioxatricyclo[5.2.2.0^{2,6}]undeca-8,10-dien-4-one

This compound was synthesized by the acetone sensitized photoaddition of dichlorovinylene carbonate to benzene as described by Hesse and Lechtken (129), and its pmr spectrum was as reported by Scharf and Klar (110); pmr (CDCl_3) δ 6.6 (m, 4H) and 4.6 (q, 2H).

Bicyclo[2.2.2]octa-5,7-diene-2,3-dione

A solution of 0.5 g 2,6-dichloro-3,5-dioxatricyclo[5.2.2.0^{2,6}]undeca-8,10-dien-4-one in 5 ml ether was added in one portion to a solution of 0.5 g KOH in 5 ml water.

The resultant two phase mixture was stirred for 1 hr at room temperature. The layers were separated, and the aqueous layer was washed, 4 x 5 ml CH_2Cl_2 . The combined organic layers were washed with 10 ml sat'd NaCl and dried (MgSO_4). Removal of solvent under reduced pressure gave 0.29 g of the title compound: mp 105-107° [Lit. (110) 107-108°].

Cyclooctatetraene oxide

A 0.25 M solution of m-chloroperbenzoic acid (34.4 g in 800 ml of chloroform) was cooled to -5° (ice-acetone bath) and one equivalent of cyclooctatetraene was added with efficient stirring dropwise via an addition funnel. The reaction mixture was stirred at -5° for one hour, stoppered, and placed in a freezer for three days at -30°. The m-chlorobenzoic acid that was formed was removed by filtration, and the chloroform solution was washed with sat'd aq. NaHCO_3 solution and dried (MgSO_4). The solution was concentrated under vacuum, and the resulting yellow oil was chromatographed on a silica gel column (50:50; hexane: pentane) giving a colorless liquid upon concentration: pmr (CDCl_3) δ 5.7-6.2 (m, 6H) and 3.58 (s, 2H); bp 73-75° (10 mm) [Lit. (60) 75-76° (12 mm)].

2,4,6-Cyclooctatrien-1-one

A procedure similar to that of Cope and Tiffany (60) was followed. A solution of 5.45 g of cyclooctatetraene oxide in 20 ml of anhydrous ether was added dropwise with stirring to a slight molar excess of LiNEt_2 in ether-pentane, which was generated from commercial $n\text{-BuLi}$ in pentane and diethylamine in ether. The temperature of the reaction mixture during the addition was not allowed to rise above -12° (Dry Ice-acetone bath). Upon completion of the addition, 10 ml of 3N aq. H_2SO_4 was added with cooling. The layers were separated, and the aqueous layer was washed three times with 15 ml of ether. The ethereal solutions were combined and washed with sat'd aq. NaHCO_3 , H_2O , and sat'd aq. NaCl and then dried (MgSO_4). The ethereal solutions were concentrated under vacuum, and the crude reaction product was purified by column chromatography on silica gel (5:95; ether:hexane) yielding a deep yellow oil upon concentration whose pmr spectrum was as reported by Barber (130): pmr (CCl_4) δ 6.97-5.50 (m, 6H), and 2.95 (d, $J = 8$ Hz, 2H); bp $46\text{-}48^\circ$ (0.8 m) [Lit. (62) $89\text{-}90^\circ$ (6 mm)].

Cyclooctatetraene oxide and DMSO

As indicated by Tsuji (93), 1 g cyclooctatetraene oxide was dissolved in 10 ml DMSO. The solution was heated on a steam bath with air bubbling through it for 24 hrs. Recovery of product as per general procedure gave only the

starting epoxide. A similar result was obtained when pure oxygen instead of air was bubbled through the solution.

Cyclooctatetraene oxide and pyridine-N-oxide

In a procedure as indicated by Oda and co-workers (94), 1.2 g cyclooctatetraene oxide (0.01 mole) and 5.7 g pyridine-N-oxide (0.06 mole) were dissolved in 20 ml CHCl_3 . The solution was heated to reflux for 15 hrs. Evaporation of the CHCl_3 under reduced pressure gave back starting materials with no evidence of reaction.

Reaction of cyclooctatetraene oxide with base and bromine

Following the procedure set forth by Stotter and Hill (95), 0.6 g of cyclooctatetraene oxide was added dropwise with stirring to an equimolar solution of lithium diethylamide (generated from commercial n-BuLi and diethylamine) in ether at room temperature. The resultant solution was stirred at room temperature for 10 min and then cooled to -78° . One equivalent of molecular bromine (0.8 g) in CH_2Cl_2 was added dropwise, and the reaction mixture was stirred for 1 min at -78° and then rapidly quenched with excess sat'd NaHCO_3 . Extraction with pentane (3 x 25 ml) gave a yellow solution which turned brown on concentration under reduced pressure and yielded a brown tar.

Bromocyclooctatetraene

A solution of 1.04 g of cyclooctatetraene (0.01 mole) in 20 ml of methylene chloride was cooled to below -55° (Dry Ice-isopropanol bath) when 0.8 g of bromine (0.01 mole) in 10 ml of methylene chloride was added dropwise with stirring. As indicated by Huisgen and Konz (131), 1.12 g of potassium t-butoxide was added in small portions and the resulting suspension was stirred at -55° for 30 minutes and allowed to stand for 2.5 hrs in a freezer at -30° , at which time the mixture had turned brown. The mixture was filtered removing a brown-white solid, and the filtrate was concentrated under vacuum to give a bright yellow oil: pmr (CCl_4) δ 5.7 (m, 7H) [Lit. (132) δ 5.5 (neat)]; bp $46-48^{\circ}$ (1.2 mm) [Lit. (131) $52.5-53^{\circ}$ (1.8 mm)].

Bromocyclooctatetraene and basic hydrogen peroxide (ethanol solvent)

According to the procedure of Fieser (133), 1.2 ml 30% H_2O_2 is added to a solution of 0.4 g anhydrous potassium carbonate in 5 ml of water, and the mixture is added to a warm solution of 0.9 g of bromocyclooctatetraene in 10 ml of 95% ethanol. The reaction mixture immediately darkened upon addition. After cooling, 20 ml of water was added, and the aqueous solution was washed (3 x 10 ml ether). The ethereal was dried (MgSO_4), and the solvent removed under reduced pressure to give a brown tar.

Bromocyclooctatetraene and basic hydrogen peroxide (benzene solvent)

The reaction was conducted as above with the use of benzene instead of ethanol as the solvent for the bromocyclooctatetraene. The two phase system was allowed to stir for 15 min at room temperature. The layers were separated, and the aqueous solution extracted with ether (2 x 10 ml). The combined organic solutions were dried (MgSO_4), and evaporation of solvent under reduced pressure again gave tar.

Acetoxycyclooctatetraene

Bromocyclooctatetraene (5.9 g) was added in one portion to a solution of 5 g AgOAc in 25 ml glacial acetic acid. The resulting reaction mixture was heated for 3 hrs at 80° . After cooling, the precipitate formed (AgBr) was removed by filtration, and the HOAc was removed under vacuum giving a yellow oil. The title compound was purified by column chromatography on silica gel (90:10; hexane:ether): pmr (CCl_4) δ 5.4-5.9 (m, 7H) and 2.01 (s, 3H) [Lit. (131) pmr (CDCl_3) δ 2.01 (s, 3H)].

Acetoxycyclooctatetraene and m-chloroperbenzoic acid

These two compounds were allowed to react at -30° in the manner as described in the production of cyclooctatetraene oxide. However, the acetate was recovered

unchanged. Reaction of these compounds at higher temperatures (in the range 25° to 75°) resulted in partial destruction of the acetate with no evidence of product formation (pmr analysis). Less starting material was recovered and more destroyed as the temperature was raised.

Acetoxycyclooctatetraene and trifluoroacetic acid

Trifluoroacetic acid generated from 90% H₂O₂ and trifluoroacetic anhydride by the method of Emmons and Pagano (134) was added dropwise with stirring to a CH₂Cl₂ solution containing an equimolar amount of acetoxycyclooctatetraene at -30° in the presence of a three fold excess of Na₂HPO₄. The mixture was stirred for 15 min at -30° after the addition was completed and the solution was filtered to remove the inorganic salts. The solution was then washed with 10% Na₂S₂O₃ and sat'd NaHCO₃ and dried (MgSO₄). Removal of CH₂Cl₂ under vacuum gave a yellow oil. Pmr analysis of this oil showed no evidence of the presence of desired products.

Methoxycyclooctatetraene

Twenty grams of bromine in 25 ml of methylene chloride were added dropwise with stirring to a solution of 13 g cyclooctatetraene in 50 ml of methylene chloride at -65°. After the mixture was stirred for 30 min at -65°, 33.8 g of dried sodium methoxide was added in small portions during

the course of 30 min, and the temperature was not allowed to rise above -50° . The mixture was then allowed to warm to about 15° , and 125 ml of dimethyl sulfoxide was added dropwise very cautiously so that the temperature did not rise above 20° (approximately 1 hr). The suspension was stirred mechanically for about 12 hrs at room temperature and then slowly poured into an ice cold solution of 36 ml of HOAc in 200 ml of water. The aqueous solution was extracted four times with 100 ml of cyclohexane. The combined organic layers were washed with sat'd aq. NaHCO_3 until neutral, then with H_2O and sat'd aq. NaCl , and dried (MgSO_4). After removal of solvent, distillation afforded 18.7 g of a yellow orange oil: pmr (CCl_4) δ 5.4-5.9 (m, 6H), 4.7 (broad s, 1H), and 3.5 (s, 3H); bp $75-79^{\circ}$ (10 mm) [Lit. (63) pmr (CDCl_3) δ 5.8 (wide m, 6H), 4.98 (broad s, 1H) and 3.56 (s, 3H); (135) bp $46-48^{\circ}$ (0.4 mm)].

Methoxycyclooctatetraene and m-chloroperbenzoic acid

The reaction was conducted in the same manner as described in the synthesis of cyclooctatetraene oxide. Work-up afforded light yellow crystals that were recrystallized from hexane and that decomposed upon standing at room temperature. Spectral data indicates that the crystals were primarily methyl 8-oxoocta-2,4,6-trienoate: pmr (CDCl_3) δ 10.2 (d, 1H, $J = 7.5$), 7.9-7.0 (m, 4H), 6.2-5.5 (m, 2H)

and 3.72 (s, 3H); mass spectrum (70 eV) m/e (relative intensity) M^+ = 166 (100), 151 (93), 134 (60) and 107 (60).

Methoxycyclooctatetraene and trifluoroacetic acid

The reaction was conducted as described above for acetyloxycyclooctatetraene and trifluoroacetic acid. Work-up afforded the yellow liquid, 2,4,6-cyclooctatrienone: pmr ($CDCl_3$) δ 6.97-5.50 (m, 6H) and 2.95 (d, 2H, $J = 8$ Hz).

Methoxycyclooctatetraene and lead tetraacetate

This reaction was performed as described in the general procedure for making acetoxy ketones using methoxycyclooctatetraene instead of a ketone. Whether the reaction mixture was refluxed for 2 days or just stirred for 30 min at room temperature, a multi-component product was obtained with no significant incorporation of an acetate group.

Pyridinium hydrobromide perbromide

The title compound was prepared by the method of Fieser (136) and recrystallized from acetic acid.

Methoxycyclooctatetraene and brominating agents

Whether methoxycyclooctatetraene was allowed to react with molecular bromine in protic (CH_3OH) or aprotic (CH_2Cl_2) solvents, with pyridinium hydrobromide perbromide by the method of Freedman and Doorakian (137), or with $CuBr_2$ by the method of Koyano (138), tars were the only isolable product.

Cyclooctatetraene, DMSO, and bromine

Addition of a DMSO solution of molecular bromine to a solution of cyclooctatetraene in DMSO, dropwise with stirring and cooling, was evidenced first by the decoloration of the first few drops of bromine solution and followed by a blackening of the solution. Recovery of the product as given in the general procedure gave only black tar. A similar result was obtained upon addition of a DMSO solution of N-bromosuccinimide to cyclooctatetraene in DMSO.

Trans-7,8-Dibromobicyclo[4.2.0]octa-2,4-diene

To a solution of cyclooctatetraene in methylene chloride (10% solution) at -55° was added an equimolar amount of bromine in methylene chloride dropwise with stirring. Concentration under vacuum gave the title compound whose pmr spectrum was as reported by Huisgen and Boche (54): pmr (CDCl_3) δ 5.5-6.2 (m, 4H), 4.96 (t, 1H), 4.65 (t, 1H), and 3.0-3.9 (m, 2H).

Trans-7,8-Dibromobicyclo[4.2.0]octa-2,4-diene and DMSO

The addition of 1 g of the above dibromide to 10 ml DMSO resulted in an immediate blackening of the solution. The reaction mixture was stirred for 15 minutes at room temperature. Recovery of the organic product as stated in the general procedure gave only black tar. The addition of excess NaHCO_3 to neutralize any HBr generated or AgClO_4

to facilitate removal of the bromide did not diminish the yield of tar.

Trans-7,8-Dibromobicyclo[4.2.0]octa-2,4-diene and sodium nitrite

One gram of the dibromide was added in one portion to a solution 0.8 g NaNO₂ in 50 ml DMF (139). The addition was marked by the immediate blackening of the solution. The reaction mixture was allowed to stir for 30 min at room temperature, and the product was recovered in an identical manner as described for DMSO solutions to give a brown tar.

Trans-7,8-Dibromobicyclo[4.2.0]octa-2,4-diene and silver nitrate

When the method of Ferris and co-workers (140) for the synthesis of alkyl nitrates from alkyl halides and AgNO₃ was applied to the above dibromide, a tar was the only isolable product.

Trans-7,8-Diacetoxycyclo[4.2.0]octa-2,4-diene

To a solution of 1.70 g AgOAc and 0.82 g NaOAc in acetic acid was added in one portion 2.64 g of 7,8-dibromobicyclo[4.2.0]octa-2,4-diene. The resulting reaction mixture was heated for 1 hr at 65° and then cooled. The precipitate formed (AgBr) was separated by filtration with the aid of celite. The acetic acid was removed under vacuum yielding white crystals that were recrystallized from acetic acid:

pmr δ 5.05-5.9 (m, 4H), 3.2-3.62 (m, 1H), 2.35-2.8 (m, 1H), 2.05 (s, 3H) and 2.0 (s, 3H); mp 59-60° [Lit. (56) mp 60-61°].

Trans-7,8-diacetoxycyclo[4.2.0]octa-2,4-diene and sodium bis-(2-methoxyethoxy)aluminum hydride (Vitride)

As indicated by Vit (107), 0.87 g (0.05 mole) of the above diacetate was dissolved in 15 ml anhydrous ether and cooled in a Dry Ice-acetone bath. Seven mls of a 70% solution of Vitride in benzene (0.05 gramatom of hydrogen) was diluted with 10 ml anhydrous ether, and the resultant ethereal solution was added dropwise with stirring to the reaction pot. The addition was evidenced by the immediate formation of a gray-white precipitate. After the addition was completed (~ 15 min), the mixture was allowed to stir at -70° for 10 min. Utilizing Fieser's (108) basic work-up for LiAlH_4 reductions (on grams LiAlH_4 - n ml H_2O , n ml 15% NaOH, and 3n ml H_2O), 0.5 ml water was added to the cold solution. The heterogeneous mixture was allowed to warm to room temperature, and 0.5 ml 15% NaOH and 1.5 ml water were added dropwise. The above quantities were determined by the fact that 1 g LiAlH_4 (M.W. 38) contains approximately 1 gramatom of hydrogen. During the course of the NaOH addition the colorless ethereal solution turned yellow. Filtration of salts gave a yellow solution, and evaporation of solvent under reduced pressure gave a yellow

solid containing an aldehyde but no acetate groups. If the acidic work-up of Capka and co-workers (141) with dilute acid (HOAc was used instead of HCl) was utilized, an aldehydic product was also obtained.

3,6-Dibromocyclohexene-1

To a solution of 4 g 1,3-cyclohexadiene in 10 ml carbon tetrachloride cooled to 0° was added 8 g Br₂ in 20 ml CCl₄ dropwise with stirring. Evaporation of the CCl₄ under vacuum gave the dibromide as an oil that was crystallized from hexane: mp 96-100° [Lit. (142) 97-103°].

Attempted addition of acetoxy ketene to 3,8-dibromocyclohexene

The procedure of Brady and Dorsey (143) was used. A solution of 0.09 moles of acetoxyacetyl chloride (obtained from K. Schmitt) in 20 ml ether was added dropwise to a mechanically stirred solution of 4.8 g (0.2 mole) 3,8-dibromocyclohexene and 0.095 mole triethylamine in 200 ml anhydrous ether cooled in a Dry Ice-ethanol bath. After the addition was completed, the cooling bath was removed, and the mixture was allowed to warm to room temperature. After 4 hrs, the salt formed was filtered with the aid of celite. Evaporation of solvent gave a crude solid. Analysis by pmr showed the solid to contain the starting dibromide and gave no evidence of an addition product.

1,5-Dichloro-2,4-dioxabicyclo[3.2.0]hept-6-en-3-one

This compound was synthesized by the acetone sensitized photoaddition of acetylene to dichlorovinylene carbonate as described by Hinshaw (109): pmr (CDCl₃) δ 6.80 (s).

α-Pyrone

Coumalic acid was pyrolyzed at 650° under high vacuum as reported by Zimmerman, et al. (144): pmr δ 7.2-7.7 (m, 2H) and 6.15-6.42 (m, 2H).

1,5-Dichloro-2,4-dioxabicyclo[3.2.0]hept-6-en-3-one andα-pyrone

These two compounds were dissolved in toluene in a 1:4 ratio, respectively. Stirring of this solution for 5 hrs at room temperature gave no reaction. Heating of this solution only resulted in destruction of the thermally unstable carbonate with no evidence of cycloaddition (pmr analysis).

2,6-Dichloro-3,5-dioxatricyclo[5.4.0.0^{2,6}]undeca-8,10-dien-4-one

This compound was made by the 2-butanone sensitized photoaddition of dichlorovinylene carbonate to benzene by the procedure and in the apparatus as described by Scharf and co-workers (111): mp 144-146° [Lit. 146°]. Hydrolysis of this compound by the two phase method (aq. KOH and

ether) as described in the synthesis of bicyclo[2.2.2]octa-5,7-diene-2,3-dione gave an intractable material.

Vinylene carbonate and benzene

The acetone sensitized photoaddition of vinylene carbonate to benzene was attempted in the same manner as described in the synthesis of 2,6-dichloro-3,5-dioxatricyclo[5.2.2.0^{2,6}]undeca-8,10-dien-4-one. A white solid was recovered and identified as the dimers of vinylene carbonate: pmr (CDCl₃) δ 7.3 (b s).

Cyclooctatetraene and chromyl chloride

Following the procedure of Sharpless and Teranishi (115), 1 g (~ 0.01 mol) of cyclooctatetraene in 50 ml reagent acetone was cooled to -70° (Dry Ice-acetone bath) and then 1.55 g (0.01 mol) CrO₂Cl₂ was added dropwise with mechanical stirring so that the pot temperature did not rise above -65°. After the addition was complete (~ 30 min), the mixture was stirred at -75° for 1 hr, allowed to warm to room temperature, and stirred for 1 hr. Then an ice cold solution of 3 g of NaHSO₃ in 100 ml of H₂O was slowly poured into the mixture, and the resultant solution was stirred for 30 min in an ice bath. This aqueous solution was washed (2 x 50 ml, ethyl acetate-hexane; 1:1). The organic phases were washed (100 ml H₂O and 100 ml sat'd NaCl) and dried (Na₂SO₄). Removal of solvent under reduced pressure gave

back about 0.9 g cyclooctatetraene. A repetition of the above procedure using a molar ratio chromyl chloride to cyclooctatetraene of 2 to 1 gave upon work-up an orange-yellow, multicomponent oil that proved unstable to standing at room temperature or purification by column chromatography of silica gel (hexane:ethyl acetate; 9:1). Pmr analysis of the crude oil showed two aldehydic resonances, δ 9.7 and 10.3, and a continuum of peaks from δ 8.2 to 2.0.

8,8-Dichlorobicyclo[4.2.0]oct-2-en-7-one

The title compound was synthesized by the addition of dichloroketene to 1,3-cyclohexadiene by the method of Corey and Ravindranathan (145): bp 72-74°/0.8 mm [Lit. (146) 73-74°/1 mm].

Reduction of 8,8-dichlorobicyclo[4.2.0]oct-2-en-7-one

The reductive method of Corey and Ravindranathan (145) was utilized. The dichloro compound was stirred with 4 eq. Zn dust in HOAc for 1 hr at 45°. A mixture of the dichloro compound and 8-chlorobicyclo[4.2.0]oct-2-en-7-one (about 1:2, respectively) was obtained which could be separated by chromatography, as indicated by Rey and co-workers (147); pmr δ 6.1-5.5 (m, 2H), 5.02 and 4.88 (pair of doublets, exo and endo Hg, $J = 2.6$ Hz), 3.8-3.0 (m, 2H) and 2.3-1.5 (m, 4H).

Bicyclo[4.2.0]oct-7-en-2-one

2-Cyclohexenone was added photolytically to 1,2-dichloroethylene, and the photoadduct was treated with ethylene glycol and a small amount of p-toluenesulfonic acid to form the ketal as described by House and Cronin (127). This crude ketal was dechlorinated by a disodium dihydronaphthylide solution in DME as stated by Scouten and co-workers (148) to give the title compound: bp 73-76°/10 mm [Lit. (146) 71-75°/8.5 mm].

3-Acetoxybicyclo[4.2.0]oct-7-en-2-one

Bicyclo[4.2.0]oct-7-en-2-one was allowed to react with Pb(OAc)₄ for three days as given in the general procedure giving endo and exo acetates: ir (neat) 1740 (ester C=O), 1715 (C=O), and 1240 cm⁻¹ (C-O-C); pmr (CDCl₃) δ 6.1-5.3 (m, 2H), 5.2-4.7 (m, 1H), 3.2-1.3 (m, 11H, acetate singlets at 2.0 and 2.07).

MS Calcd. for C₁₀H₁₂O₃: 180.0786

Found: 180.0791

Bicyclo[4.2.0]oct-4-en-3-one

This compound was synthesized by the method of Farrissey (89, 149) by the oxidation of 1,5-cyclooctadiene and subsequent thermolysis of the ketonic products: bp 64-69°/0.8 mm [Lit. (149) 61.5-69.5/0.9 mm].

2-Acetoxybicyclo[4.2.0]oct-4-en-3-one

Bicyclo[4.2.0]oct-4-en-3-one was allowed to react with $\text{Pb}(\text{OAc})_4$ for three days as given in the general procedure. Purification via column chromatography on silica gel (hexane:ethyl acetate; 9:1) separated the acetoxy ketone from the starting ketone: ir (neat) 1745 (ester C=O), 1685 (C=O), 1615 (C=C) and 1230 cm^{-1} (C-O-C); pmr (CDCl_3) δ 6.85 and 6.10 (AMX, 2H, $J_{\text{AM}} = 10\text{ Hz}$, $J_{\text{AX}} = 4.5\text{ Hz}$ and $J_{\text{MX}} = 1.2\text{ Hz}$), 5.42 (d, 1H, $J = 8.1\text{ Hz}$), 3.4-1.7 (m, 6H) and 2.12 (s, 3H).

MS Calcd. for $\text{C}_{10}\text{H}_{12}\text{O}_3$: 180.0786

Found: 180.0794

5,8-Dibromocycloocta-1,3-diene

This compound was synthesized by the bromination by N-bromosuccinimide of 1,5-cyclooctadiene in carbon tetrachloride following the procedure of Cope and co-workers (150): bp $92-96^\circ/0.8\text{ mm}$ [Lit. bp $95-105^\circ/1\text{ mm}$].

6-Bromocycloocta-2,4-dien-1-one

Five grams of 5,8-dibromocycloocta-1,3-diene were dissolved in 50 ml DMSO containing a three fold excess of solid NaHCO_3 . The reaction mixture was allowed to stir for three days at room temperature after which time the salt was filtered and the product recovered from the DMSO as per general procedure giving a brownish oil. Purification via

column chromatography on silica gel (9:1; hexane:ether) gave pure bromoketone: ir (neat) 1665 (C=O) and 1635 cm^{-1} (C=C); pmr (CCl_4) δ 6.8-5.5 (m, 4H), 5.0-4.5 (m, 1H), and 3.2-2.0 (m, 4H); mass spectrum (70 eV) $\underline{m/e}$ (rel intensity) 202 and 200 (20), 160 and 158 (76), 121 (89), 120 (80), and 91 (100).

2,6-Cyclooctadienone

This compound was synthesized from 1,5-cyclooctadiene by the method of Cantrell and Solomon (151): bp 45-48°/0.8 mm [Lit. 42-44°/0.4 mm].

2,6-Cyclooctadienone and lead tetraacetate

The reaction of these two compounds was carried out as described in the general procedure for 6 days gave an acetoxy ketone along with the starting ketene. The acetoxy ketene could be purified by column chromatography on silica gel (9:1; hexane:ethyl acetate) and was shown to contain only one component by glpc and tlc analysis. The esr spectrum of this product defined its structure as 4-acetoxy-cycloocta-2,7-dien-1-one (vide infra): ir (neat) 1750 (C=O ester), 1690 and 1665 (C=O), 1648 (C=C), and 1250 cm^{-1} (C-O-C); pmr (CDCl_3) δ 6.6-5.3 (m, 5H) and 3.2-1.7 (m, 7H, acetate singlet at 2.1).

MS Calcd. for $\text{C}_{10}\text{H}_{12}\text{O}_3$: 180.0786

Found: 180.0796

Dimethyl 1,4,5,6-tetramethylbicyclo[2.2.0]hex-5-ene-2-endo, 3-endo-dicarboxylate

A solution of 25 g of 2-butyne in 25 ml of methylene chloride was added slowly to a stirred suspension of AlCl_3 (31.2 g) in 50 ml of methylene chloride at $0-5^\circ$. The mixture obtained was slowly added to 33.3 g of dimethyl maleate in 50 ml of methylene chloride at -5° , followed by the addition of a solution of 50 ml of dimethyl sulfoxide and 50 ml of methylene chloride. The reaction mixture was poured into ice water (600 ml), and the aqueous layer was washed with pentane. Following the removal of solvent, the residue oil was hydrolyzed with 66 g KOH in 300 ml H_2O at 30° for 3 min causing selective hydrolysis of the excess dimethyl maleate. The title compound was obtained by extraction with pentane followed by purification on a silica gel column (90:10; hexane:ethyl acetate): pmr spectrum was as reported by Koster and co-workers (117): (CCl_4) δ 3.57 (s, 6H), 3.08 (s, 2H), 1.57 (s, 6H), and 1.11 (s, 6H).

Dimethyl 1,4,5,6-tetramethylbicyclo[2.2.0]hex-5-ene-2-endo, 3-endo-dicarboxylate and the acyloin condensation

The acyloin condensations were run using sodium-potassium alloy as the reducing agent as in the general procedure described by Whittle (81). When trimethylchlorosilane was used as a trapping agent, mixtures of

bis-siloxylethers were obtained under the conditions of refluxing xylene, room temperature in anhydrous ether, and -10° in anhydrous ether. When t-butyldimethylchlorosilane was used as a trapping agent at room temperature in anhydrous ether, dimethyl 1,4,5,6-tetramethylbicyclo-[2.2.0]hex-5-ene-2-endo, 3-exo-dicarboxylate was the major isolable product (about 90%) of the reaction. The pmr spectrum agrees with that determined by Koster and co-workers (117): δ 3.68 (s, 3H), 3.61 (s, 3H), 3.36 (d, 1H, $J = 6$ Hz), 3.03 (d, 1H, $J = 6$ Hz), 1.60 (s, 3H), 1.47 (s, 3H), 1.18 (s, 3H), and 0.92 (s, 3H).

3,8-Dibromocyclooct-5-ene-1,2-dione

The above compound was made by cupric bromide bromination of cyclooct-5-ene-1,2-dione utilizing the procedure of Kowar (80). The pmr spectrum agrees with that obtained by Kowar: (CDCl_3), δ 6.07 (m, 2H), 5.15 (ABX quartet, 2H), and 2.90 (m, 4H).

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ACKNOWLEDGEMENT

First, I would like to thank Professor Glen A. Russell for his support and for the opportunity of working with him and also the members of the old Kinstle group and of the Russell group, particularly John Gerlock and Chuck Tanger, for their cooperation and invaluable aid. I would also like to express my appreciation to the Chemistry Department for the offer of an instructorship that allowed me to continue my graduate career uninterrupted. Finally, the debt I owe to my parents for their countless sacrifices and to my wife, Sharon, for the happiness and the little joys that she has brought into my life can never be repaid.