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Electron spin resonance studies of the valence isomerism of 1,4- semidiones

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Electron spin resonance studies
of the valence isomerism of 1,4-semidiones

by

Charles Michael Tanger

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
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DOCTOR OF PHILOSOPHY

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Major: Organic Chemistry

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Ames, Iowa

1976

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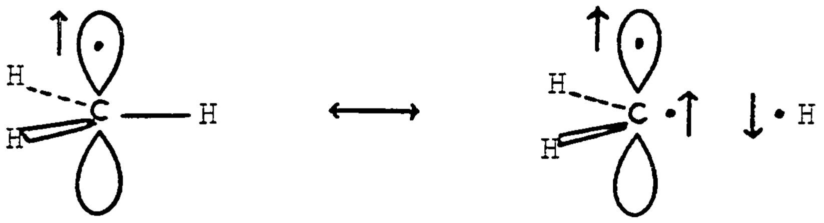
INTRODUCTION

One-electron reduction of conjugated diketones gives rise to radical anions which are called semidiones, in analogy to the radical anions of quinones, called semiquinones. Since they have one unpaired electron, semidiones are paramagnetic and have had considerable utility as a spin label in electron spin resonance (esr) studies. The generation, properties, and applications of semidione spin labels have been reviewed in detail (1,2,3,4). The semidione spin label has been used to study both cyclic and acyclic conformational equilibria, the structure of naturally occurring ketones, and the mechanisms of unpaired electron spin propagation, i.e., the interaction of the unpaired electron with σ and π electrons in the molecule.

There are fundamentally two mechanisms of spin propagation, spin polarization and delocalization (e.g., conjugation, hyperconjugation, etc.), which may operate simultaneously or independently as geometry and orbital symmetry allow.

The spin polarization mechanism transfers the spin of an unpaired electron in a p or π orbital of an sp^2 hybridized atom to sigma-bonded nuclei in the nodal plane. The magnitude of

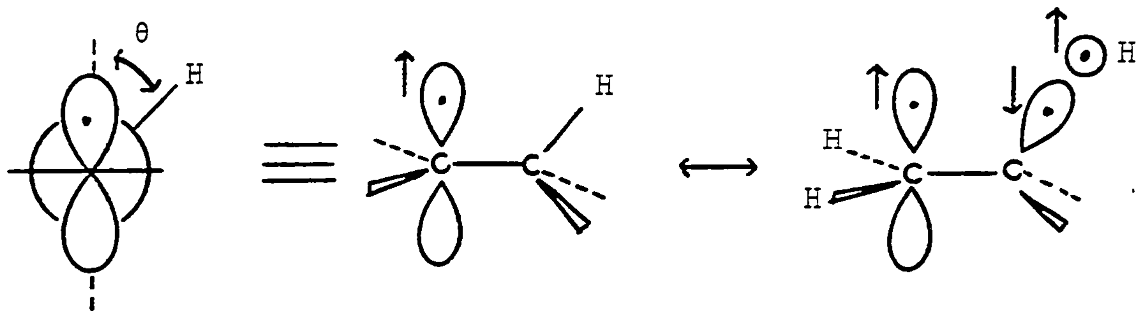


the coupling for a sigma-bonded hydrogen to an sp^2 carbon is given by Equation (1) where a_{σ}^{H} is the coupling constant of the

$$a_{\sigma}^{H} = Qp_{n} \tag{1}$$

hydrogen atom, p_n is the spin density on the carbon atom, and Q is an empirical constant between -20 and -30 which varies with the charge and bond angles of the sp^2 hybridized carbon atom (5). p_n for sp^2 centers in extended π systems may be calculated using the McLachlan technique (6). This mechanism introduces a spin on the sigma-bonded atom opposite in sign to that on the trigonally hybridized atom due to a greater repulsion of the electron of opposite sign in the sigma bond by the unpaired electron in the π orbital as a result of electron exchange coupling.

The hyperconjugation mechanism transmits spin to atoms adjacent to a p or π orbital containing an unpaired spin and is a function of the dihedral angle θ. The hyperfine coupling



constant for an adjacent hydrogen atom is given by Equation (2)

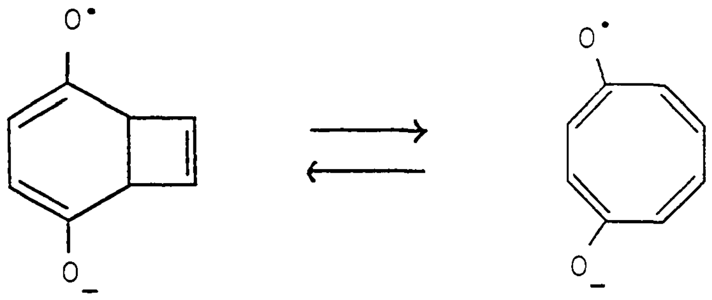
$$a^H = (B_o + B \cos^2\theta)p_n \qquad (2)$$

where B_o is usually a negligible constant, B is 40 for radical ions, θ is the dihedral angle, and p_n is again the spin density on the sp^2 carbon (7,8).

From Equation (2) it is seen that the interaction between the unpaired electron and the adjacent nucleus will be greatest when θ is 0° and will be negligible when θ equals 90°. For systems in which the dihedral angle varies with time due to inversion or rotation, an average value for $\cos^2\theta$ must be used. Hyperfine splitting falls off rapidly as the distance from the paramagnetic center increases resulting in small or negligible coupling of hydrogen atoms β or γ to the paramagnetic center. However, large long range hyperfine splitting can be observed in rigid molecules in which orbital interaction is maximized (1,2,3,4).

The sensitivity of hyperfine splitting to geometry and spin density should make it a useful tool for the detection of rearrangements in semidione radical anions. Indeed, a number of such observations have been reported, _vide infra_.

The objective of this work was the generation of the semidiones _1_ and _2_ in order to observe their possible interconversion _via_ valence isomerization.



1 ⇌ 2

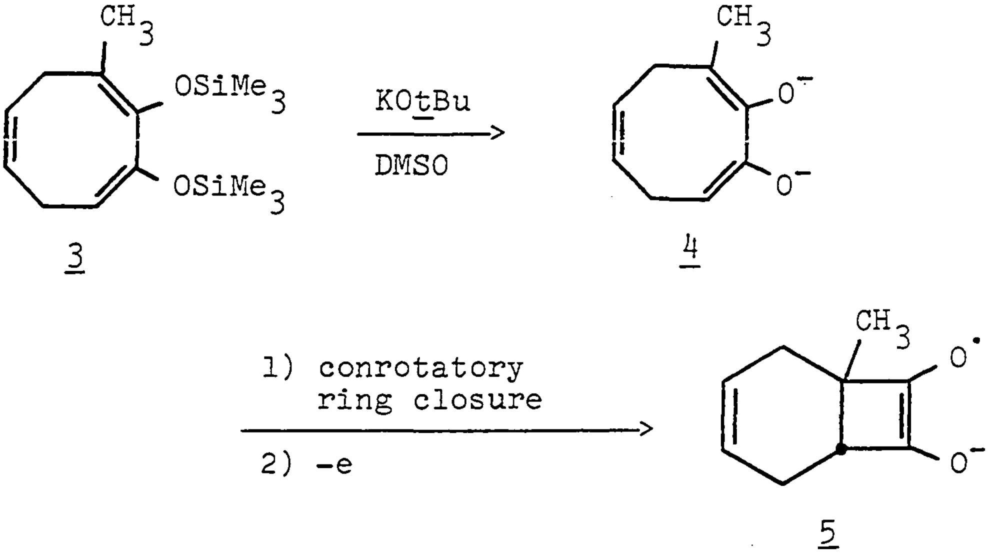
Throughout the remainder of this work, the following conventions will be used when referring to esr experiments. Hyperfine splitting constants (hfsc, a^H) are in gauss (G). "Potassium t-butoxide" will be used interchangeably with "base" and "B^-".

HISTORICAL

ESR Studies of Valence Isomerism

Valence isomerizations are isomerizations which proceed without migration of atoms or groups of atoms (9). If the process is dynamic, it is termed valence tautomerism (10). The subject is of considerable interest to organic chemists and has been well reviewed by Maier (11).

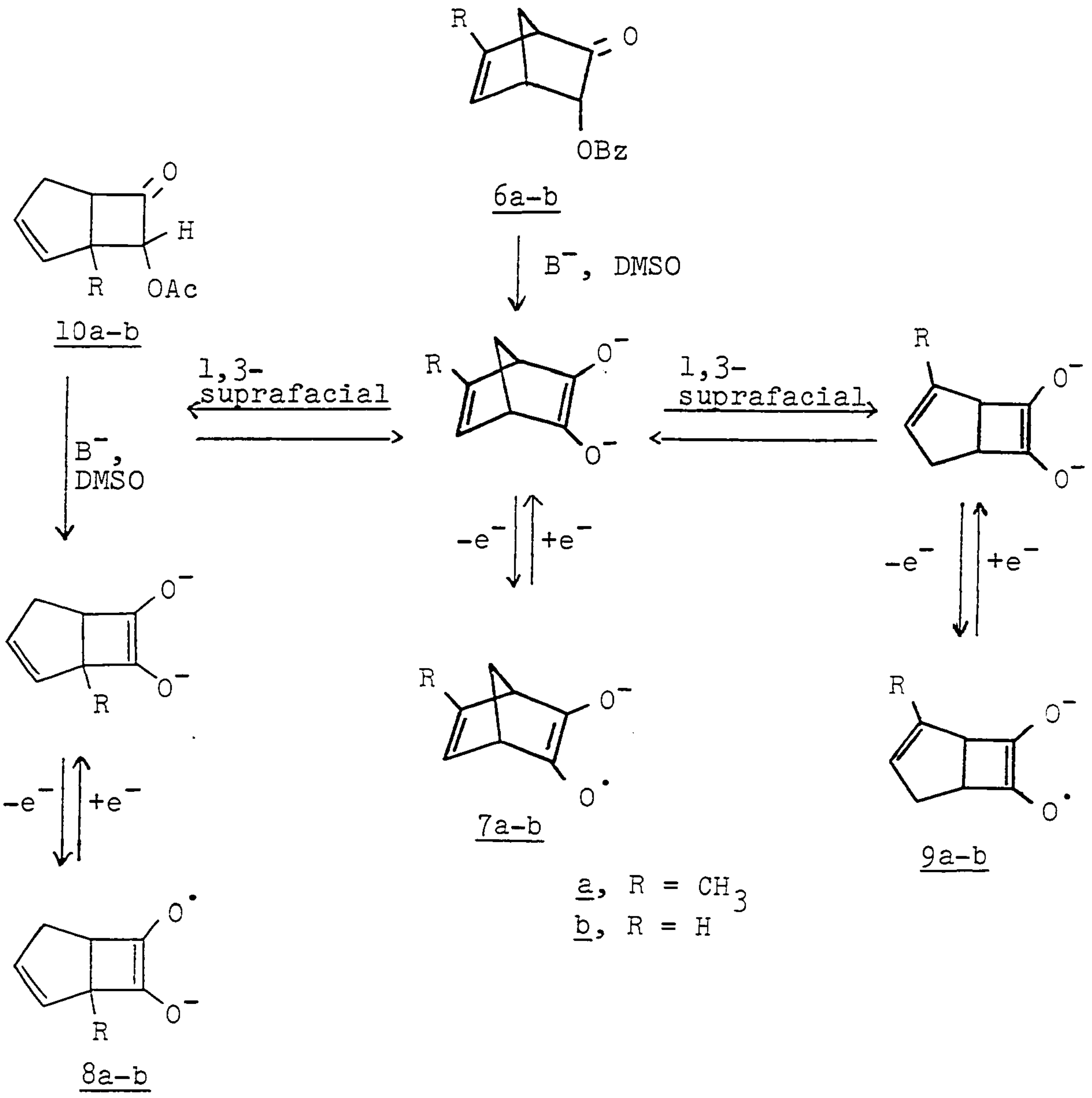
The first report describing the detection of valence isomerization of radicals by esr appears to be that of Russell and Whittle (12). Treatment of cyclooctatriene 3 with potassium t-butoxide in dimethylsulfoxide (DMSO) gives an esr signal consistent with semidione 5, which is presumably



derived from conrotatory ring closure of dianion 4 and subsequent one-electron oxidation.

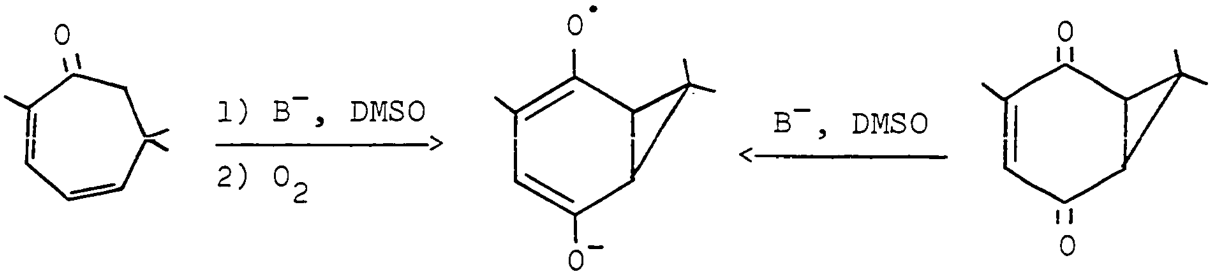
Since this earliest report, the Russell group at Iowa State has reported a number of rearrangements or valence isomerizations of semidiones or dianions detectable by esr. Semidiones derived from bicyclo[2.2.1]heptene-2-one precursors were found to be in equilibrium with those of bicyclo[3.2.0]-heptenes (13,14,15). Thus, treatment of 6a with base in DMSO (Scheme 1) gives a mixture of semidiones 8a and 9a. Acetoxy

Scheme 1



ketone 10a gives a mixture of semidiones 8a and 9a under the same conditions. Although 7a is not observed for this system, treatment of unsubstituted 6b (or acetoxy-, or dimethyl-*tert*-butylsiloxy analogues) gives an esr signal which indicates the presence of both the bicyclo[2.2.1]- and bicyclo[3.2.0]-semidiones. The data are consistent with rearrangement *via* the dianions rather than the radical anions.

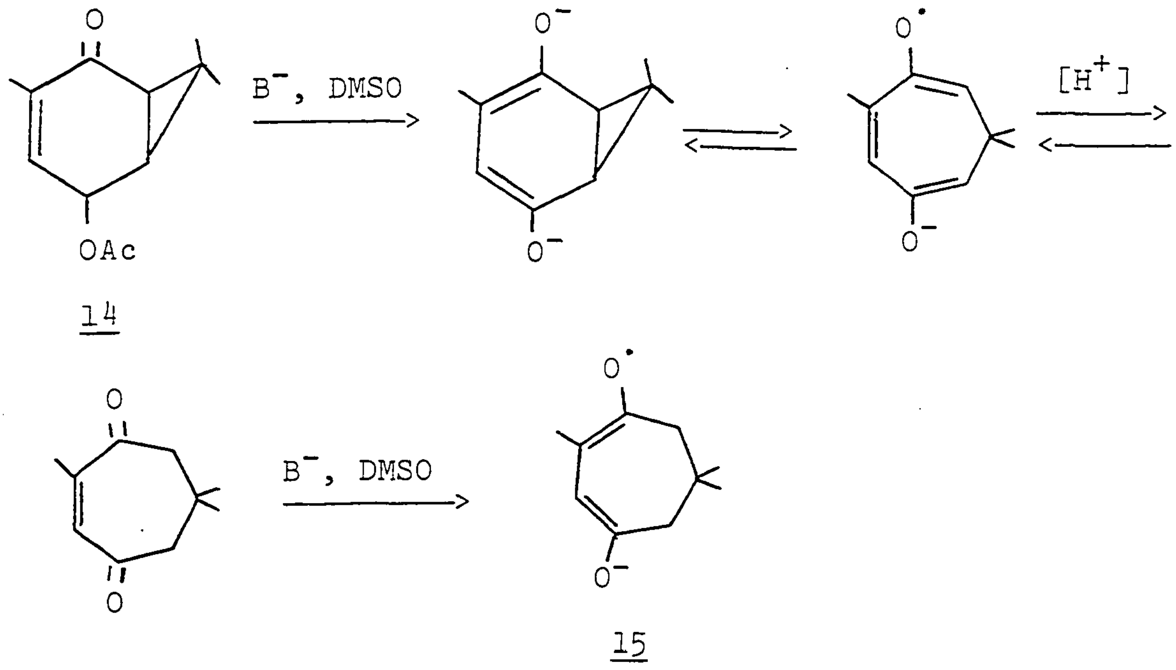
Eucarvone (11) and 3,7,7-trimethylbicyclo[4.1.0]hept-3-ene-2,5-dione (12) both give semidione 13 (16); however, the isomerization of 11 probably takes place before formation of the semidione or dianion.



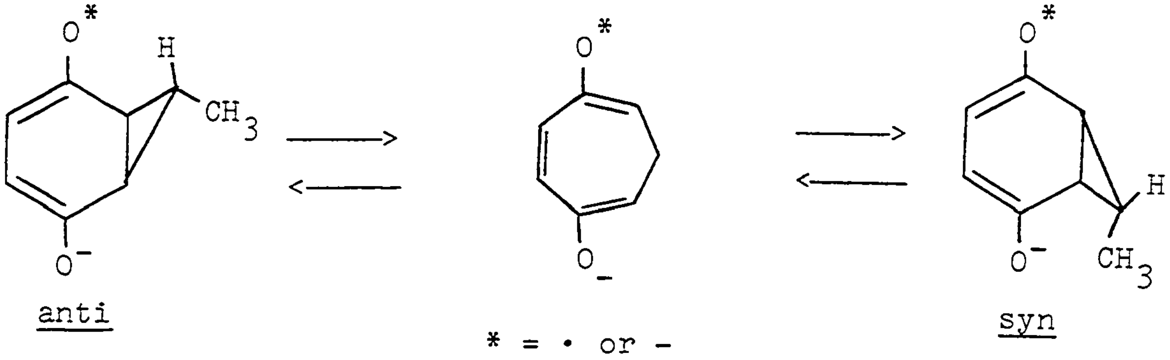
11 13 12

Valence isomerization between the dianions has been implicated in the generation of semidione 15 from the bicyclic acetoxy ketone 14 (17) (Scheme 2).

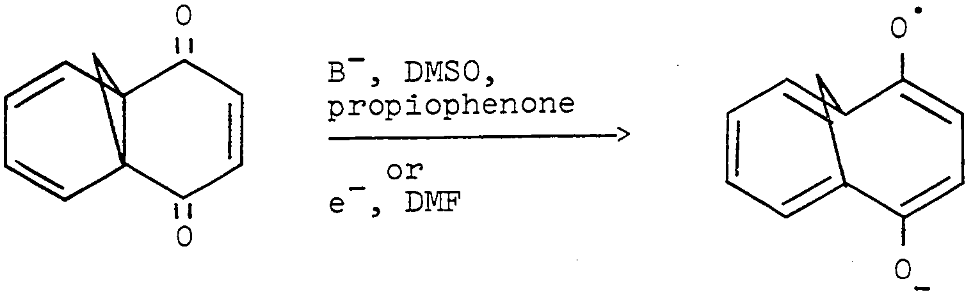
Scheme 2



It has been observed that both anti and syn-7-methylbicyclo[4.1.0]heptene-2,5-dione give the same 95:5 ratio of the corresponding anti- and syn-semidiones in base and DMSO (18). This result, combined with the observation that the ratio of the anti- and syn-semidiones is a function of time and extent of electrolytic reduction (18), appears to support a dynamic valence isomerization between radical anions or dianions.



The tricyclic diketone 16 gives bicyclic semidione 17 upon either chemical (16) or electrolytic (19) reduction.



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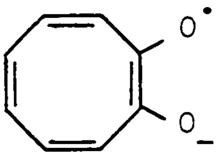
17

A number of attempts have been made to prepare cyclooctatriene-1,2-semidione 18 or its bicyclic isomer 19, which



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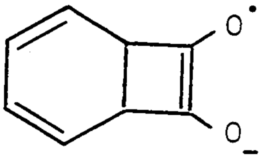
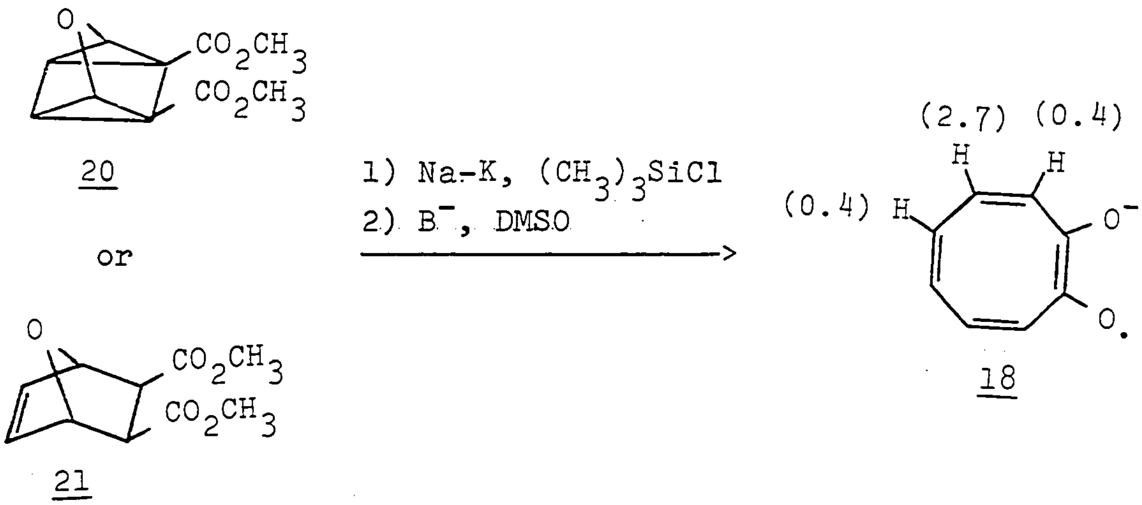


19

are positional isomers of the semidiones 1 and 2.

Whittle reported that diesters 20 and 21 give the same esr signal with splitting from four hydrogens of 0.5 gauss and splitting from two hydrogens of 2.7 gauss (20). The data are consistent with a rearrangement of the initially formed



product of the acyloin condensation to 18. Extended Hückel calculations for planar 18 predict a_{α}^{H}, $a_{\gamma}^{H} >> a_{\beta}^{H}$, whereas INDO calculations on nonplanar 18 predict $a_{\alpha}^{H} > a_{\beta}^{H}$, a_{γ}^{H}.[1]

Reduction of cis-1,2-dimethylcyclohexa-3,5-diene-1,2-dimethyldicarboxylate (22) gives two different paramagnetic species whose concentrations depend on the extent of reduction (21). Thus, treatment of 22 with sodium-potassium amalgam in dimethoxyethane (DME) for short periods of time gives an esr signal consistent with the monocyclic semidione 23. More extensive reduction gives rise to a new signal at the expense of the old consistent with the

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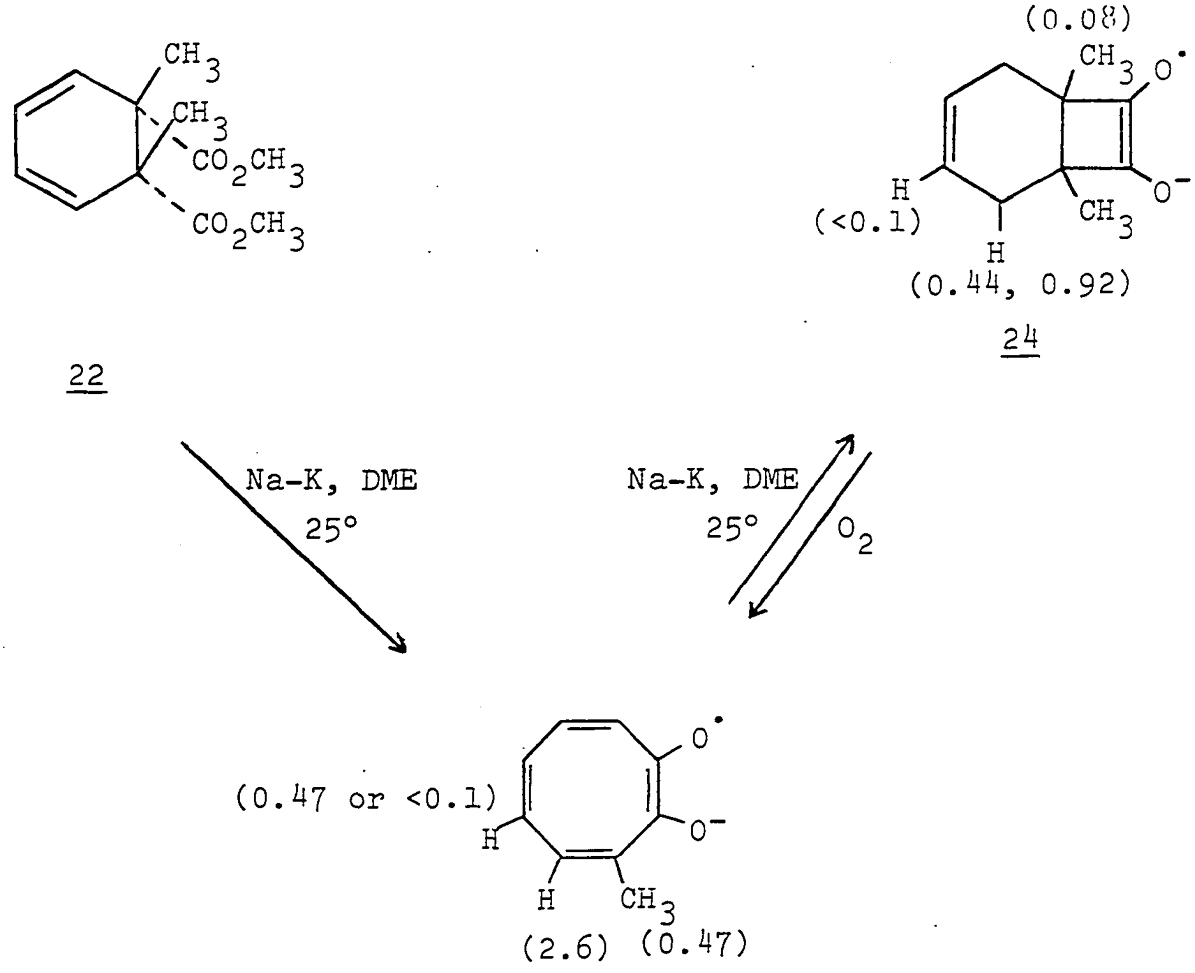
[1] C. S. C. Chung, private communication, Iowa State University, Ames, Iowa, 1974.



22

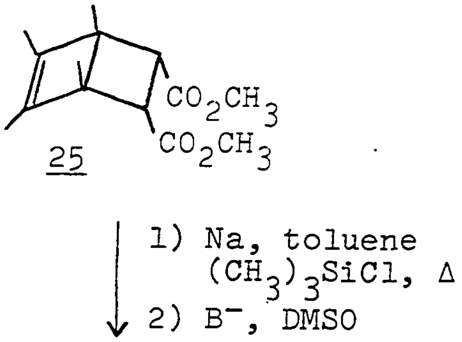
24

23

bicyclic semidione 24. Addition of traces of oxygen converts 24 to 23.

The acyloin condensation of diester 25 followed by treatment of the crude reaction product with base and DMSO gives an esr spectrum in which four sets of hfsc's, A-D, (Scheme 3) can be seen (22).

Scheme 3



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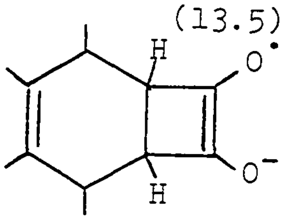
A a^H = 13.5 (2H)



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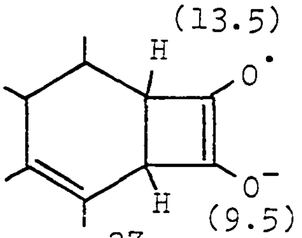
B a^H = 13.5 (1H) and 9.5 (1H)



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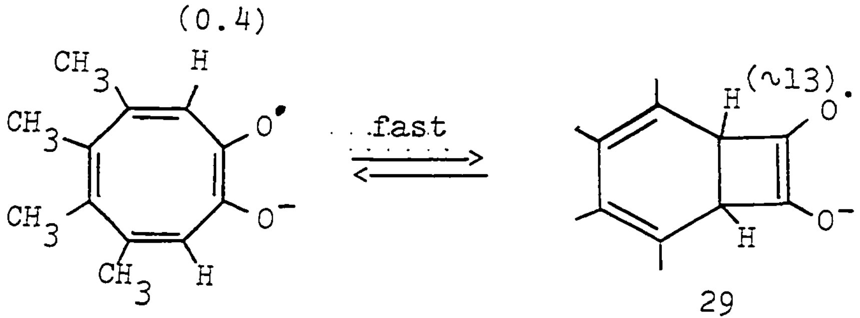
C a^H = 9.3 (2H), unassigned

D a^H = 7.2 (2H), $a^H_{CH_3}$ = 0.48 (6H), and 0.24 (6H)



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29

Assignment of structures 26 and 27 to the observed coupling constants indicated is straightforward. The signal for two equivalent hydrogens with splitting constant of 9.3 gauss is unassigned. The fourth signal is somewhat perplexing. The splitting constant of 7.2 gauss for two hydrogens is much too large for 28 on the basis of the INDO and Hückel calculations, and the work of Whittle (20) and Siddens (21) previously cited. On the other hand, 7.2 gauss is too small for the alpha hydrogens of cyclobutane semidione 29 which are expected to be 10-14 gauss (2,3,4).

A reasonable explanation is that the semidiones 28 and 29 are in rapid equilibrium resulting in a time-averaged coupling constant of 7.2 gauss.

Other attempts to prepare semidiones 18 and 19 have been documented (22).

The 1,4-semidiones 1 and 2 are in theory related to the 1,2-semidiones 18 and 19 and also to the known bicyclooctadiene-1,2-semidione (32)[2] by the rearrangements shown in Scheme 4. However, while Scheme 4 provides some entertaining possibilities, it is highly unlikely that intermediates 30

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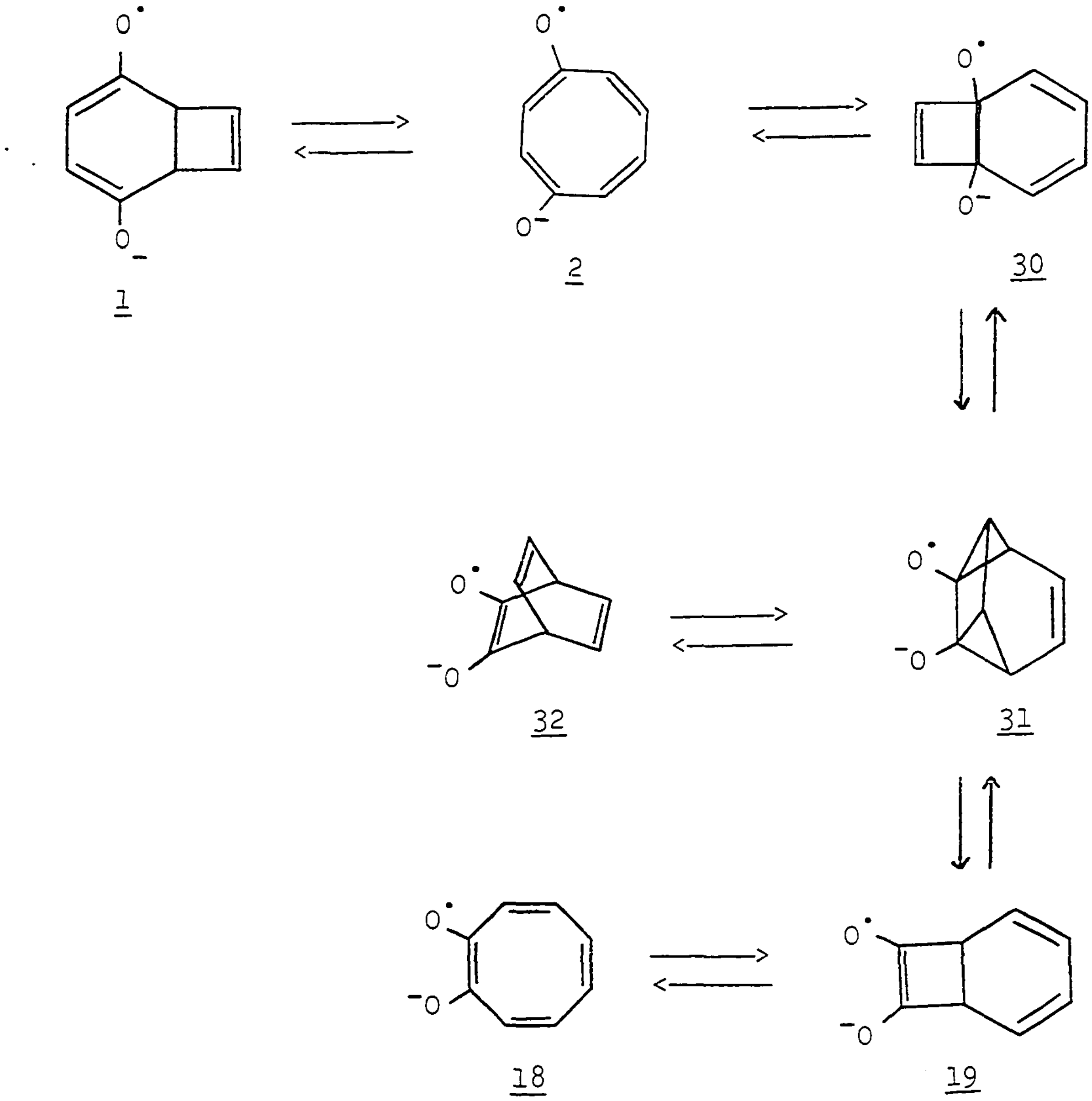
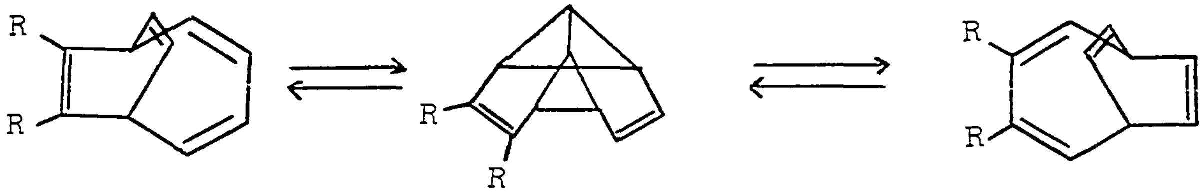
[2] R. L. Blankespoor, private communication, Wake Forest University, Winston-Salem, North Carolina, 1974.

Scheme 4

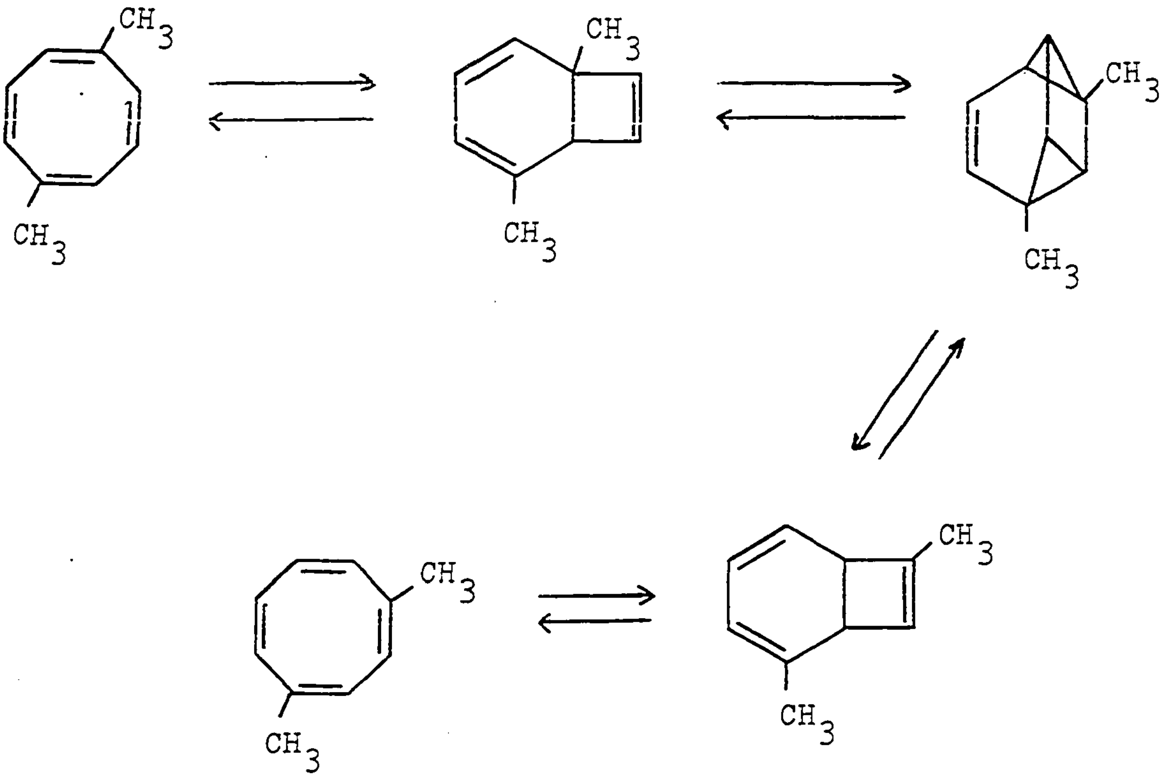


and 31 would be formed since in all cases their formation would involve destruction of the π orbital system stabilizing the semidione precursor.

The intramolecular Diels-Alder reaction involved in going from 30 to 31 is not without precedent. Intramolecular Diels-Alder reactions have been implicated in the automerization of bicyclo[4.2.2]deca-2,4,7,9-tetraenes (23) and also in the



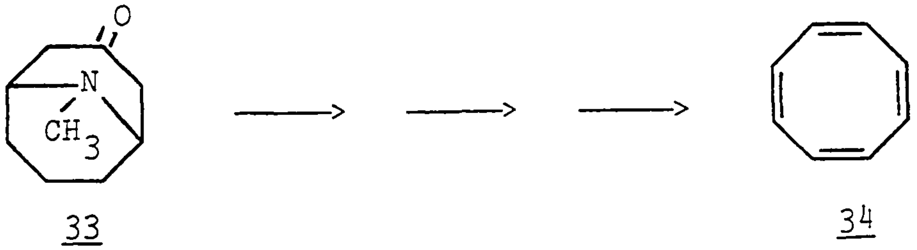
positional isomerization of dimethylcyclooctatetraenes (24).



Cyclooctatetraene

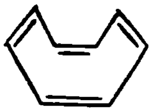
Due to the similarity of the canonical structure of 1,4-semidione 2 to that of cyclooctatetraene (34), some discussion of cyclooctatetraene is warranted. The chemistry of cyclooctatetraene is well reviewed (25,26,27).

Cyclooctatetraene was first synthetized by Willstätter and Waser from pseudopelletierine (33) in 1911 by a laborious thirteen step synthesis (28). Reppe and coworkers developed a practical synthesis in which cyclooctatetraene could be



obtained in commercial quantities by the nickel catalyzed tetramerization of acetylene (29). With practical quantities available the chemical and physical properties of cyclooctatetraene were thoroughly investigated.

For the most part, the chemical reactions of cyclooctatetraene are those of a highly unsaturated olefin (25,26,27). The physical properties, including the ultraviolet (30), infrared (31), and the proton magnetic resonance spectra (32) are in accord with the electron diffraction data (33,34,35) which indicate that cyclooctatetraene exists in a D_{2d} "tub" conformation 35 and not in a planar form which Hückel (36)



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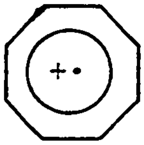
and SCF MO calculations (37) predict to be unstable. Planar cyclooctatetraene is a transition state for ring inversion (38, 39) and bond shift isomerization (39,40,41) of cyclooctatetraene itself. The bond alternating planar transition state for ring inversion is of approximately 2 kcal less energy than the equal bond length transition state for bond shift isomerism.

Whereas cyclooctatetraene itself is not planar, its radical anion and dianion, easily generated by either electrolysis (42) or chemical reduction with alkali metals (43), are. The esr spectrum of the radical anion (44,45) and the pmr (46), infrared (47), and ultraviolet spectra (47) of the dianion are consistent with planar aromatic structures.

The radical cation (36) and dication (37) of cyclooctatetraene have received less attention than the anions.



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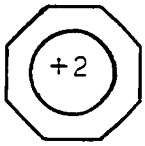
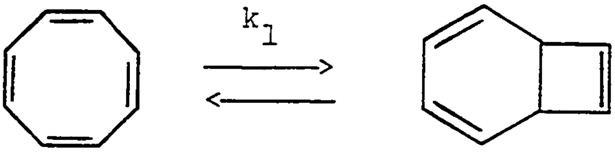


37

Attempts to prepare (48) or detect (49,50) the dication are inconclusive. The radical cation 36 has been observed by esr (51). The spectrum is consistent with a nonplanar structure, in agreement with calculations (37).

The Cyclooctatetraene - Bicyclo[4.2.0]-octa-2,4,7-triene Equilibrium

After discovering the synthetic reaction making cyclooctatetraene available in large quantities, Reppe and coworkers studied its chemistry in detail (29). The reaction of cyclooctatetraene with dienophiles gives adducts which are best explained as arising from the bicyclic triene 38.

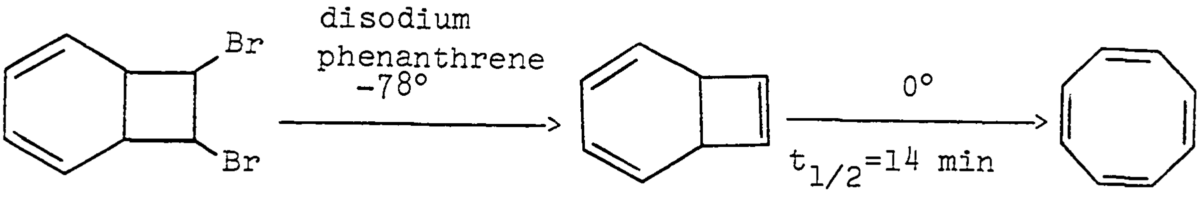


35 38

Whether cyclooctatetraene actually existed in equilibrium with the bicyclic isomer 38 or whether the tetraene and the dienophile underwent rearrangement within a collision complex remained an open question for more than a decade (52,53,54).

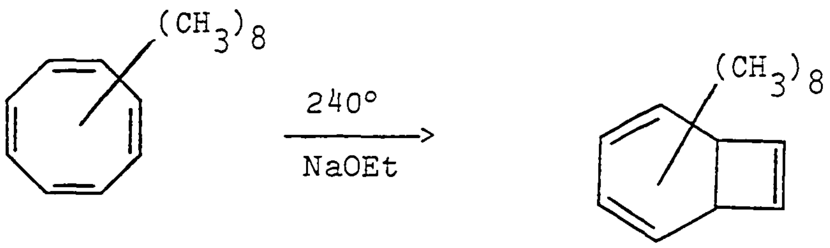
Huisgen and coworkers studied the kinetics of the reaction of cyclooctatetraene with dienophiles dilatometrically and established that cyclooctatetraene (35) and bicyclo[4.2.0]-octa-2,4,7-triene (38) are true valence tautomers (55,56). At 100° in dioxane the equilibrium concentration of 38 is only .01%. The energy of activation for isomerization of cyclooctatetraene is 27.4 kcal mol^{-1} with a rate constant, k_1, of 69.4 x 10^{-5} ℓ mole^{-1} sec^{-1} at 105°.

Vogel and coworkers were able to prepare 38 by reduction of the vicinal dihalide 39 with disodium phenanthrene at low temperatures (57). The triene 38 is stable at low temperatures but isomerizes to cyclooctatetraene as the temperature is raised. The half-life of 14 minutes for isomerization at 0° indicates an energy of action for the isomerization of 18.7 kcal mol^{-1}.



39 38 35

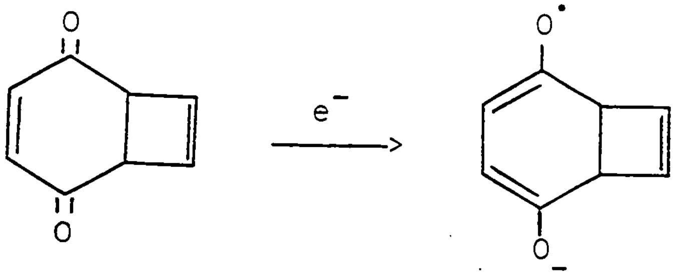
The bicyclic triene 38 has also been reported as a product of the photochemical irradiation of cycloocta-tetraene (58,59). A report that octamethylcyclooctatetraene is irreversibly isomerized to its bicyclic isomer by heating with sodium ethoxide (60) has been retracted (61).



DISCUSSION

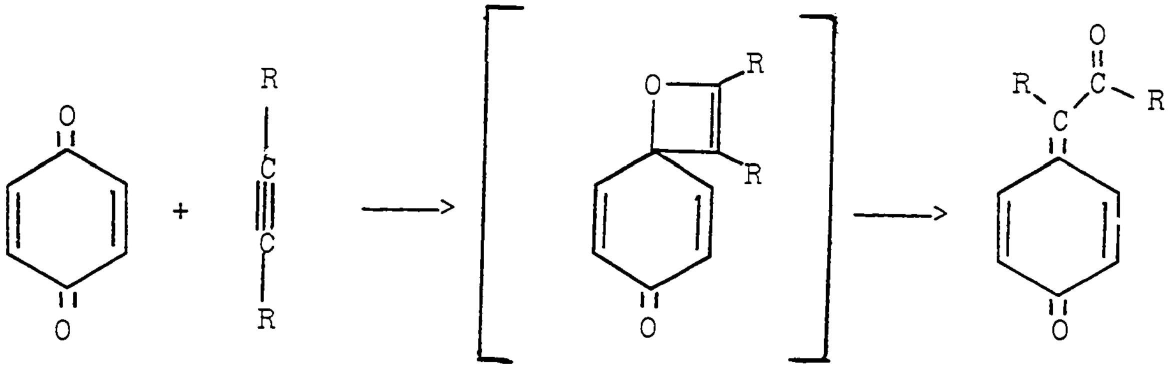
Synthesis of Bicyclo[4.2.0]octa-3,7-diene-2,5-diones

Bicyclo[4.2.0]octa-7-ene-2,5-semidione 1 is the one-electron reduction product of bicyclo[4.2.0]octa-3,7-diene-2,5-dione (40), which at the inception of this work was an unknown compound.



40 1

The most obvious route to this compound, the [2+2] photoaddition of acetylene to benzoquinone, is unfeasible.



Photolysis of solutions of benzoquinone and acetylenes yields products derived solely from the addition of the acetylene across the carbonyl rather than the olefinic bond (62,63). However, Pappas and coworkers have shown that 2-methoxy-p-benzoquinone adds acetylenes to the activated olefinic bond to give the bicyclic diene-diones in good yield (64,65). 1,4-Naphthoquinones, whether activated by substitution at the ortho position or not, add acetylenes across the olefinic bond (along with varying degrees of carbonyl addition) upon irradiation (64,65,66,67,68,69).

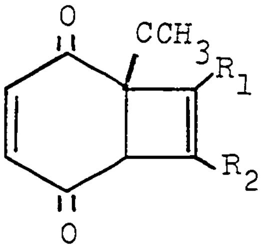
A number of the 2-methoxybenzoquinone and naphthoquinone acetylene adducts were obtained for esr studies (Table 1).

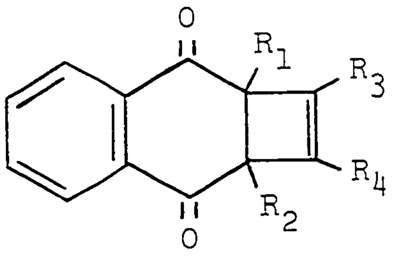
Since the photochemical addition of quinones and acetylenes is useless for the synthesis of the unsubstituted bicyclo[4.2.0]octa-3,7-diene-2,5-dione (<u>40</u>), an alternate synthesis was devised (Scheme 5).

Cyclohex-2-ene-1,4-dione monoethylene ketal (<u>46</u>) was synthesized in a manner similar to that reported for its 5-methyl and 5-phenyl derivatives (70). Thermal cracking of monoketal <u>45</u> to give <u>46</u> was a capricious reaction requiring three or four distillations to achieve complete cracking and resulted in variable yields. The overall yield for the six steps leading to ketal <u>48</u> was 31%.

It was at this point that the synthesis hit a snag. The ketal <u>48</u> proved exceptionally difficult to hydrolyze. Treatment of <u>48</u> under a variety of hydrolysis conditions (protic

Table 1. Photochemical adducts of quinones and acetylenes[a]





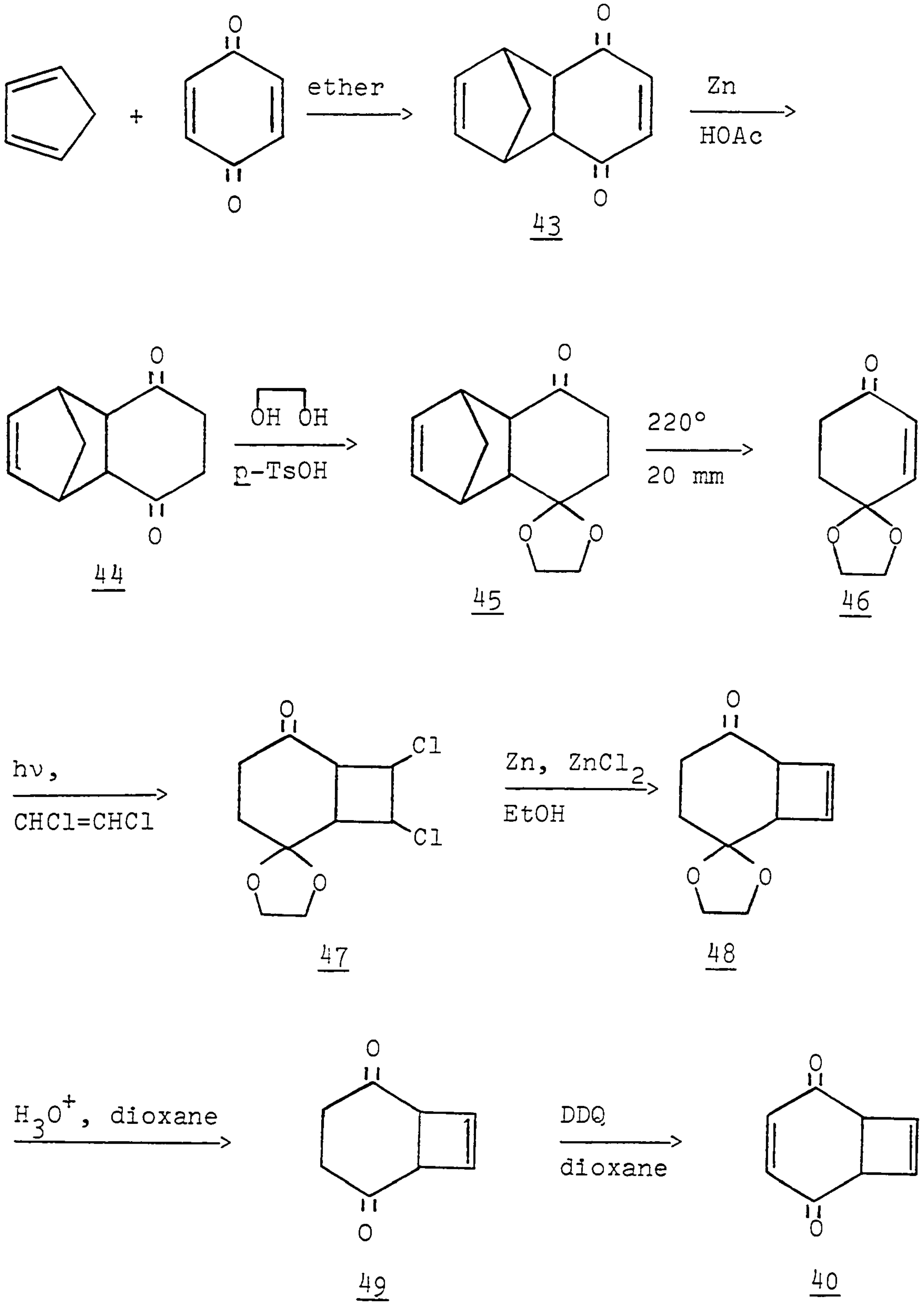
	R_1	R_2
41a	Ph	H
41b	Ph	CH_3

	R_1	R_2	R_3	R_4
42a	H	H	Ph	Ph
42b	OCH_3	H	Ph	Ph
42c	OCH_3	H	Ph	H
42d	H	H	CH_3	CH_3
42e	CH_3	CH_3	CH_3	CH_3
42f	CH_3	CH_3	Ph	H

---

[a] Samples 41a-b and 42a-c were provided by Professor S. P. Pappas, North Dakota State University, Fargo, North Dakota.

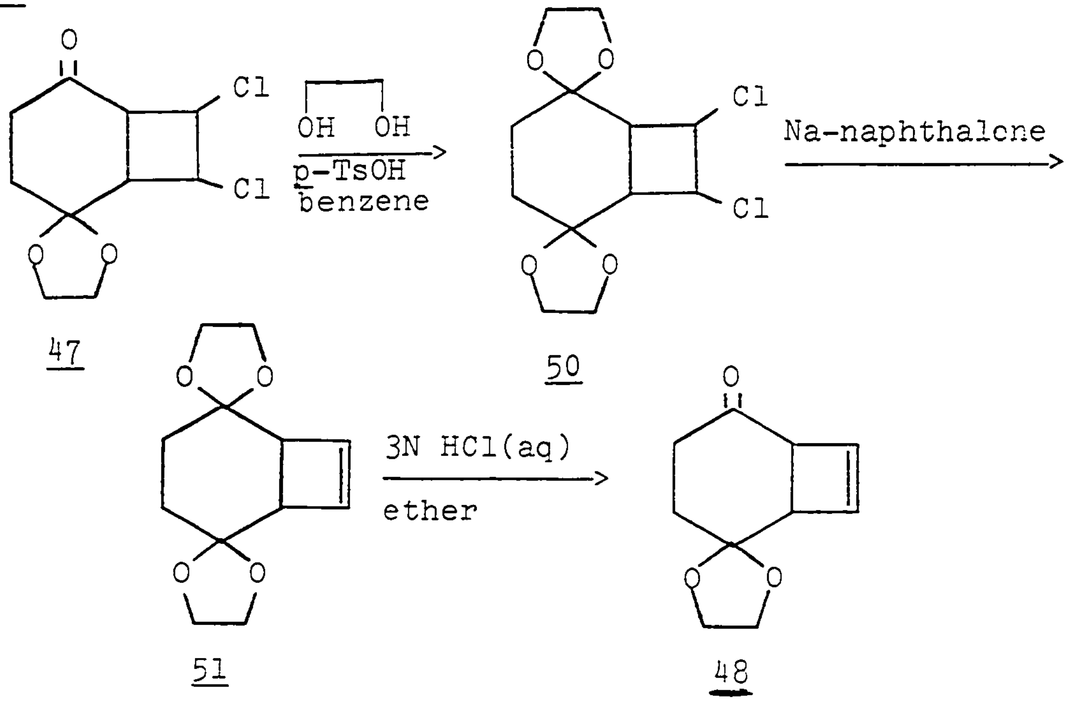
Scheme 5


ether
43
Zn
HOAc
44
OH OH
p-TsOH
45
220°
20 mm
46
hν,
CHCl=CHCl
Cl
Cl
47
Zn, ZnCl2
EtOH
48
H3O+, dioxane
49
DDQ
dioxane
40

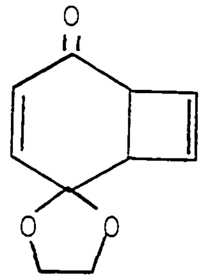
and aprotic catalysts, one- and two-phase solutions, extended reaction times, and ketal acceptors like pyruvic acid) resulted in a thirty per cent conversion to dione 49, at best, along with what appeared to be condensation or rearrangement products. Separation of 49 and recovery of 48 could be accomplished by silica gel chromatography. More forceful hydrolysis methods resulted in complete reaction of ketal 48; however, the yield of 49 did not improve while that of the side products did.

Steric hindrance is certainly not the cause of difficulty in the hydrolysis since diketal 51, synthesized *via* an alternate route to dione 49 which used sodium dihydronaphthylide as a reducing agent, was completely hydrolyzed to monoketal 48 under mild conditions (Scheme 6).

Scheme 6



Since dione 49 was available in only limited quantities, no attempt was made to oxidize with DDQ. Ketal 48 was treated with DDQ with the hope of obtaining a more readily hydrolyzable ketal 52, but the reaction was unsuccessful.

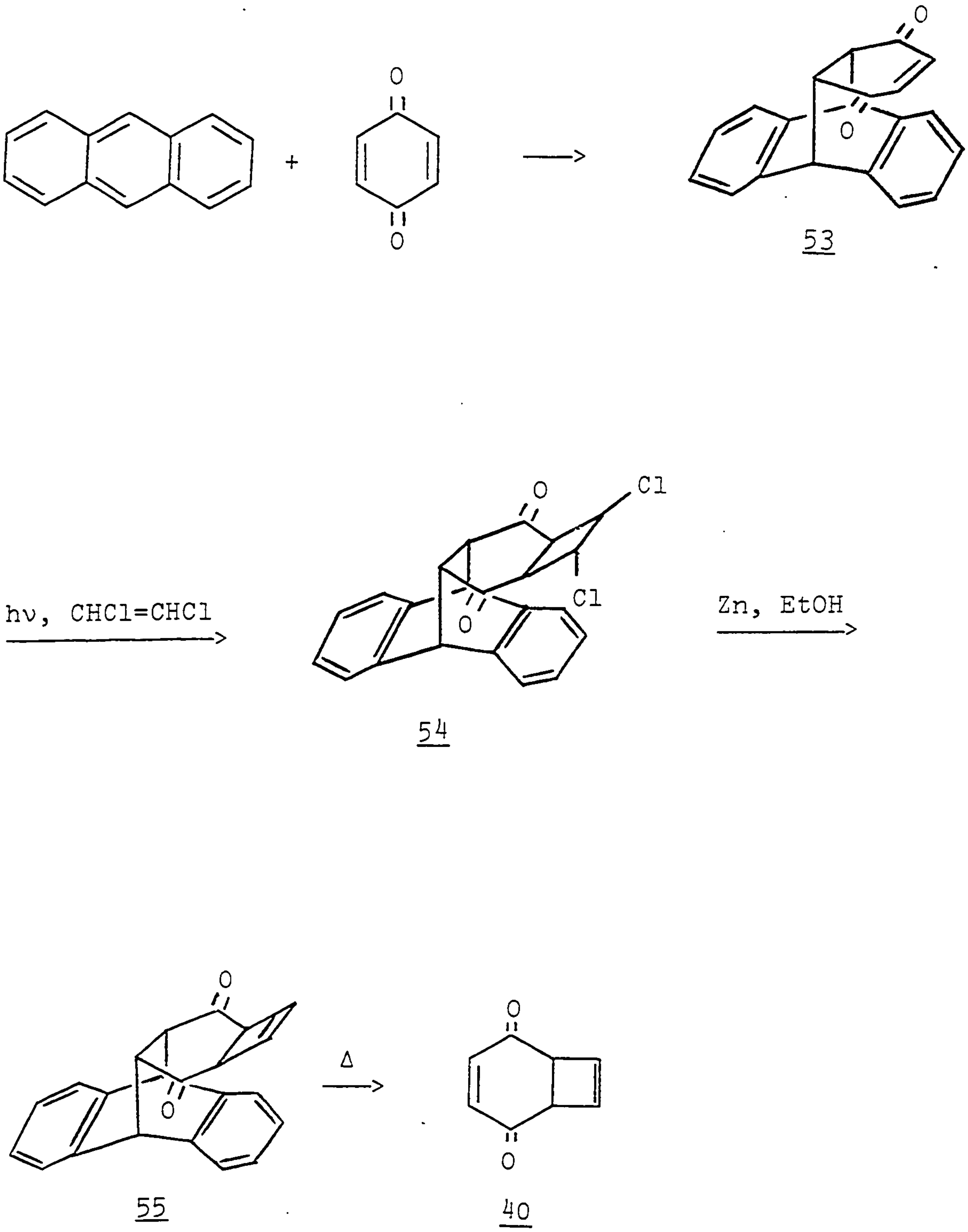


52

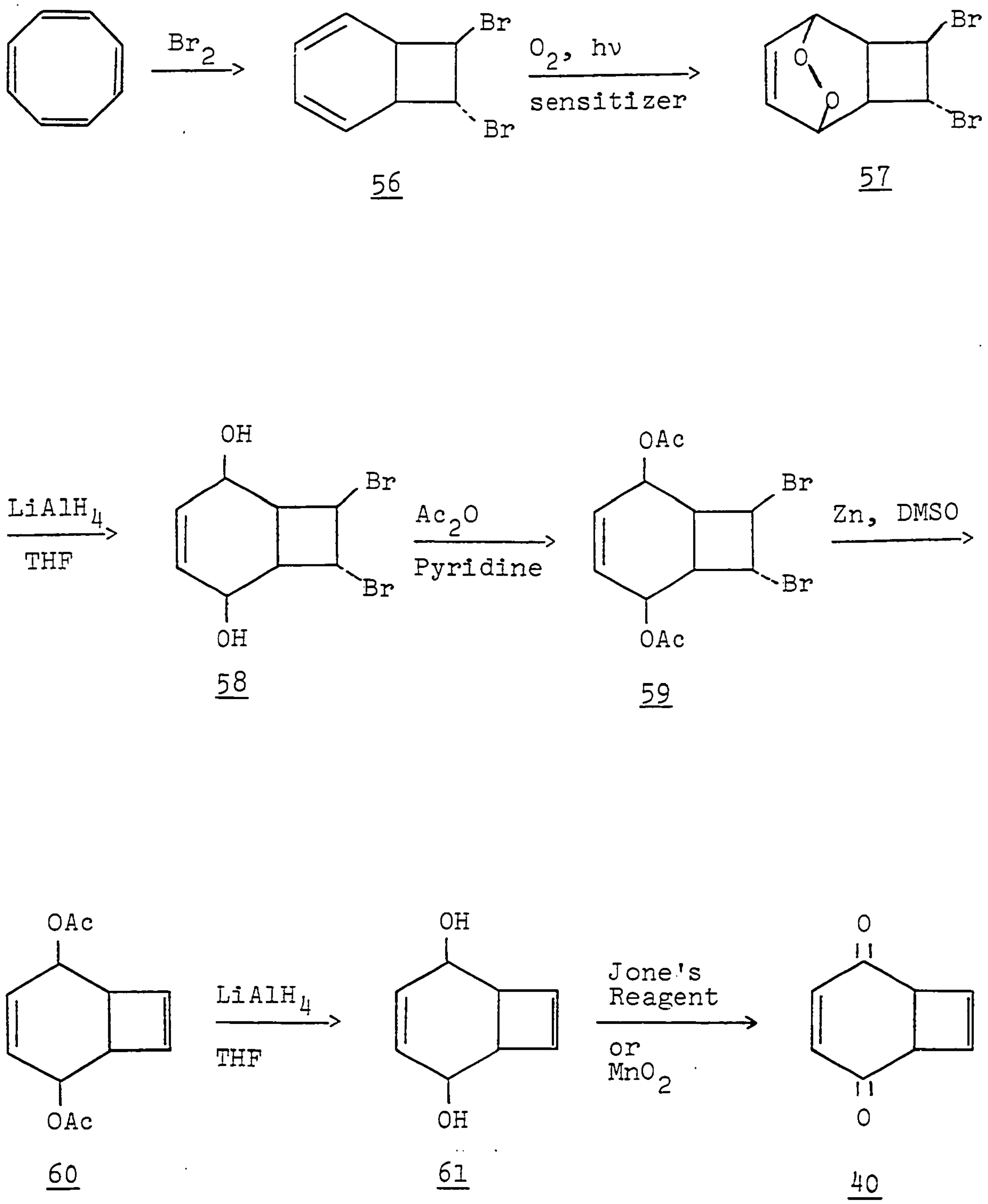
While this work was in progress, two syntheses of bicyclo[4.2.0]-3,7-diene-2,5-diones appeared in the literature. In order to modify the quinone chromophore and favor photochemical addition across the ethylene bond, Yates and Nair (71) prepared the Diels-Alder adduct of benzoquinone and anthracene (53). Photochemical addition of acetylenes followed by thermolysis gave good yields of the bicyclic diene-diones, but only products of substituted acetylene additions were reported. Our attempts to prepare dione 40 by a modification of this method were unsuccessful (Scheme 7).

Bicyclo[4.2.0]-3,7-diene-2,5-dione (40) was finally prepared following the method reported by Oda and coworkers (72) (Scheme 8).

Scheme 7



Scheme 8



56

57

58

59

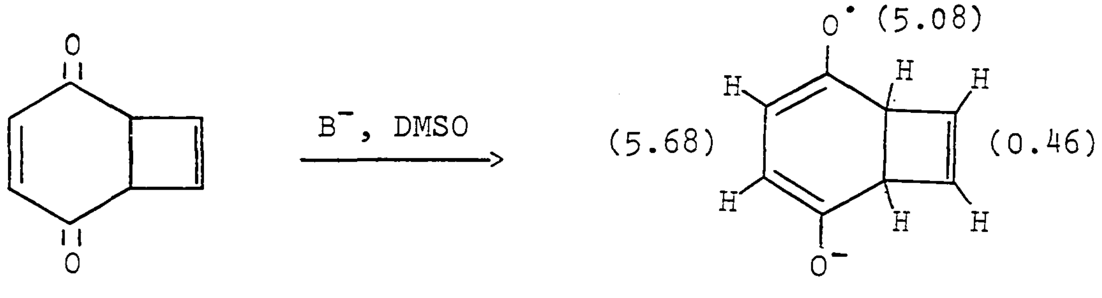
60

61

40

Bicyclo[4.2.0]octa-7-ene-2,5-semidiones

Treatment of bicyclo[4.2.0]octa-3,7-diene-2,5-dione (40) with potassium *t*-butoxide in nitrogen deoxygenated DMSO gave an esr signal consistent with bicyclo[4.2.0]octa-7-ene-2,5-semidione (1), a^H = 5.68 (2H), 5.08 (2H), and 0.46 (2H) G (Figure 1). Semidione 1 generated in this manner decayed to an undetectable concentration in 15 to 20 minutes; however, if the sample was pump-freeze-thaw degassed, the signal was stable for at least one hour. The signal generated from 40 by electrolytic reduction was identical in all respects to that generated chemically.



40

1

The observed hfsc's are in fair agreement with those calculated by the EH-SCF method.[3] The best agreement

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[3] C.S.C. Chung, private communication, Iowa State University, Ames, Iowa, 1974.

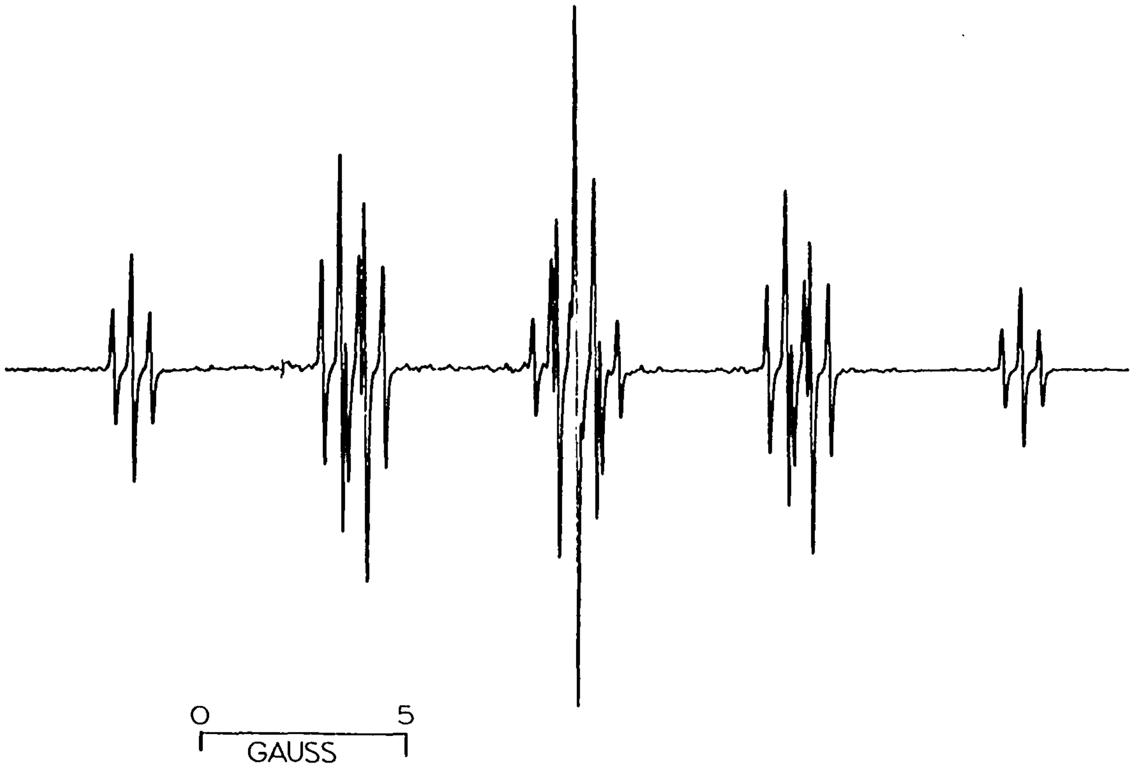
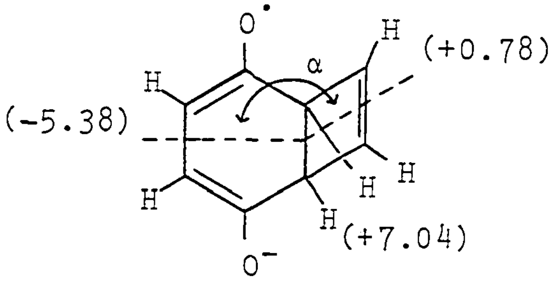


Figure 1. The first derivative esr spectrum of bicyclo[4.2.0]octa-7-ene-2,5-semidione (1) in DMSO.

between the calculated and observed hfsc's was when α was taken as 125°.



1

Generation of semidione 1 in basic d_6-DMSO gave an esr spectrum (Figure 2) which indicated exchange at the ring juncture hydrogens to be a slow process. Assuming that the outermost peaks of the new signal (arrows, Figure 2) were those of the semidione with only one hydrogen exchanged for deuterium, comparison of the calculated spectrum width (Table 2) with that measured allowed the hyperfine splitting constant (hfsc) of 5.08 gauss to be assigned to the hydrogens on the ring juncture.

Addition of small amounts of oxygen to a solution containing 1 resulted in a gradual decrease of 1 with simultaneous increase of a new radical whose signal is shown in Figure 3. The new signal, a^H = 2.46 (2H), and 1.93 (4H) G, was assigned to semiquinone 62 by analogy to previous observations for the related cyclobuta[b]-naphthalene-3,8-semiquinone (73), vide infra. Semiquinone

Figure 2. The first derivative esr spectrum of bicyclo[4.2.0]-octa-3,7-diene-2,5-dione (40) in basic d_6-DMSO after 10 minutes.

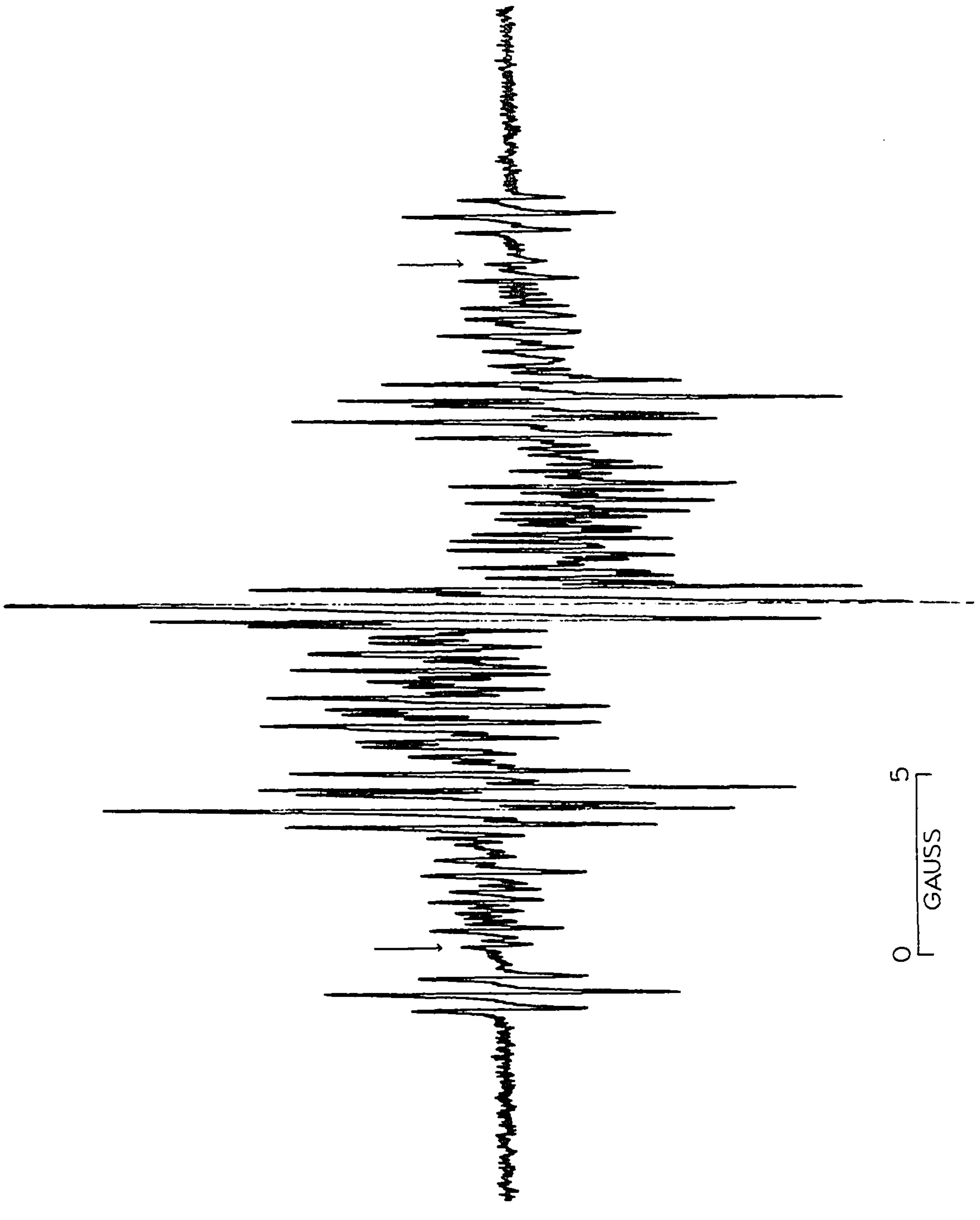

0
GAUSS
5

Table 2. Calculated spectrum widths for deuterium exchange of semidione 1 in d_6-DMSO[a,b]

	hfsc 1	$a^H = 5.08$ exchanged	$a^H = 5.68$ exchanged
	0.46 gauss	0.46 gauss	0.46 gauss
	0.46	0.46	0.46
	5.08	1.52	5.08
	5.08	5.08	5.08
	5.68	5.68	1.71
	5.68	5.68	5.68
Spectrum width	22.45	18.89	18.47

Measured spectrum width = 18.90 gauss

---

[a] The total spectrum width is the sum of the hfsc.

[b] For purposes of spectrum width calculation $a^D = \frac{a^H}{6.66} \times 2$ (6.66 is the most appropriate value for semidiones of this structure).

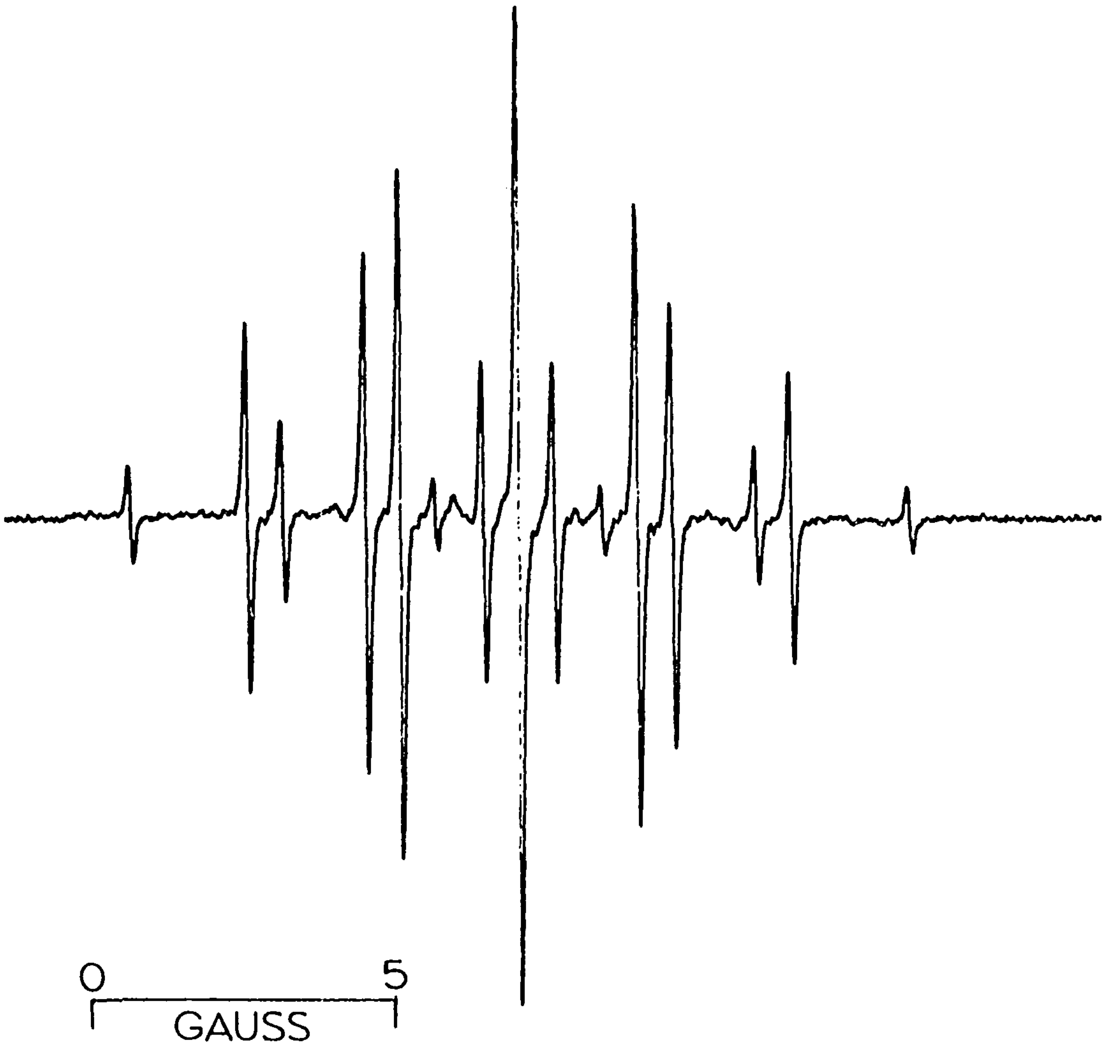
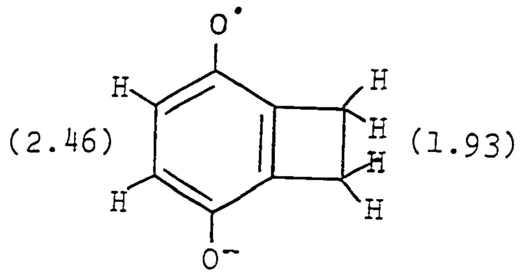


Figure 3. The first derivative esr spectrum of semiquinone 62 obtained by treating semidione 1 with air.



62

62 was stable for periods of up to one day and appreciable exposure to oxygen was required to destroy its esr signal. A discussion of the mechanism of this transformation will be deferred until later in this section.

At no time during the observation of semidione 1 was there any indication of an equilibrium between it and any other radical under ambient conditions. However, irradiation at 2537Å of a solution of 1 directly in the esr cavity caused an immediate and rapid decrease in signal intensity. Upon cessation of irradiation, an esr signal reappeared (Figure 4) which appeared to be a mixture of 1 and a new signal to which belong the outermost triplets. The high degree of overlap and low intensity make a definitive solution difficult. A possible solution with a^H = 5.17 (4H), 5.44 (2H), and 0.49 (2H) G also appears in Figure 4. Irradiation of 1 through a Pyrex filter had no effect upon the signal.

The presence of two additional hydrogens and the attending loss of unsaturation tend to rule out bicyclic

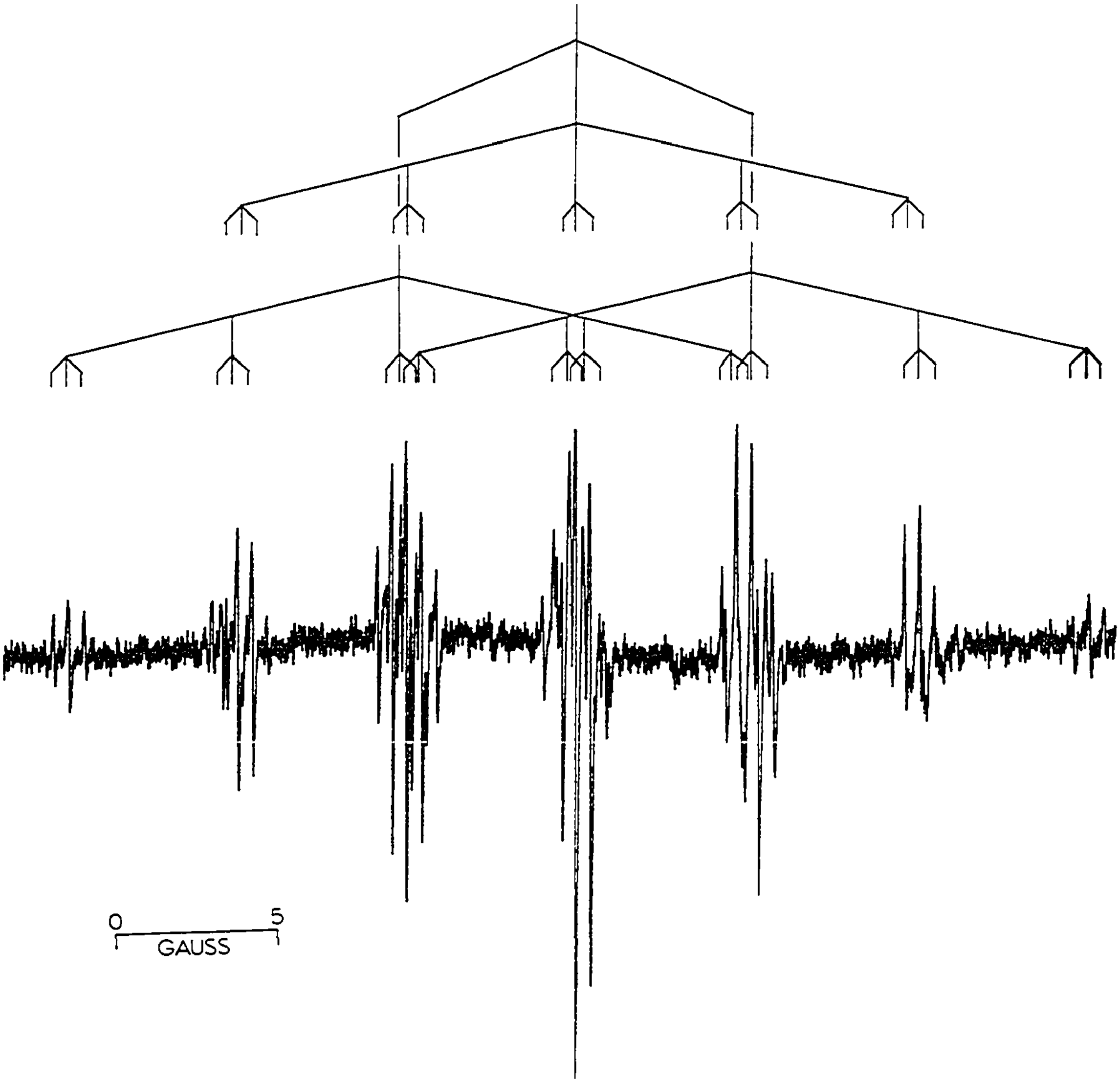
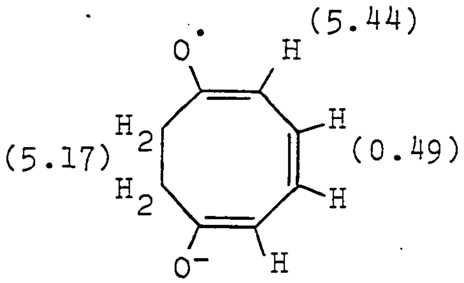
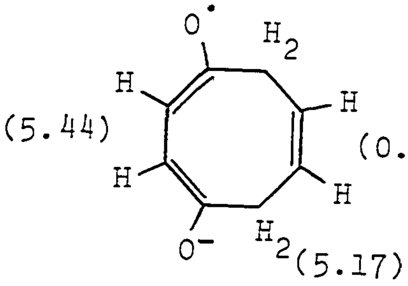


Figure 4. The first derivative esr spectrum recorded after photolysis of a solution of semidione 1 in the esr cavity.

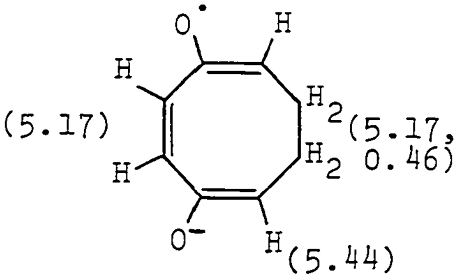
species. Monocyclic semidiones 63, 64, and 65 are possibilities.



63

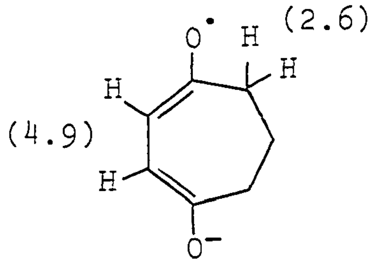


64



65

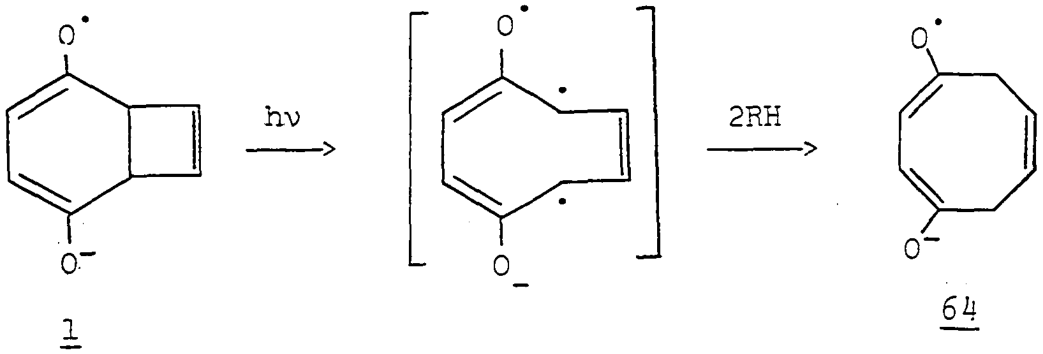
Structure 63 may be ruled out by evidence to be presented later. The homoaromatic structure 65 would certainly experience a great deal of strain in achieving planarity. Of these structures 64 appears most reasonable, although speculative. The magnitude of the hfsc's for the hydrogens on the spin label (C-2, C-3) are typical of those of 1,4-semidiones (e.g., 1). Examination of Prentice-Hall molecular models indicates that the relative geometries of the remote double bond and the spin label in 1 and 64 are nearly identical, which would account for the identical coupling constants. The anomaly of 64 is the high value of the hfsc's for the alpha hydrogens when compared to 1,4-cycloheptane semidione (66) (74).



66

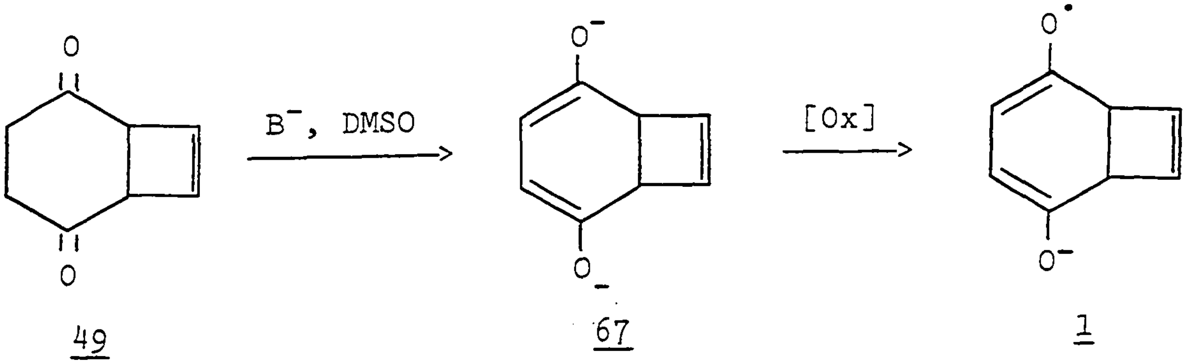
A possible mechanism for formation of 64 is shown in Scheme 9. It will be shown in a later section that the formation of 64 from the monocyclic 1,4-dione 2 or dianion is not consistent with experimental observations made with these substances.

Scheme 9



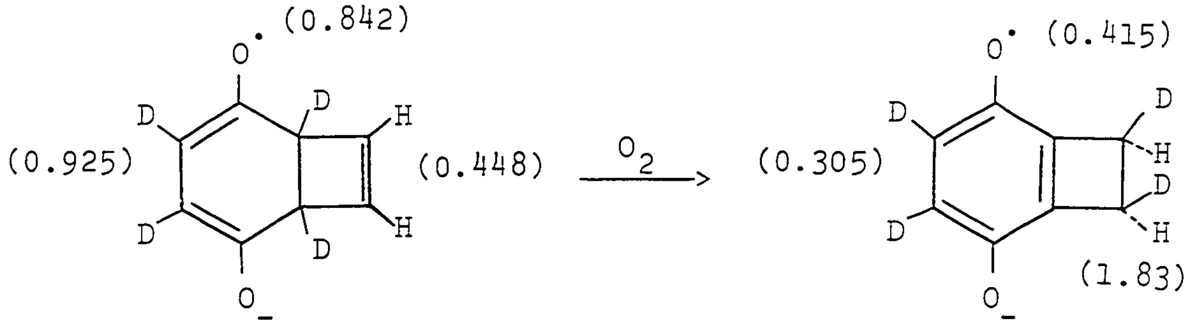
Semidione 1 could also be generated from dione 49 by treatment with potassium t-butoxide in nitrogen degassed DMSO. The signal of 1 was very much stronger than that generated from dione 40 and was stable for several hours. It will be remembered that 1 generated from 40 required freeze-pump-thaw degassing to exhibit extended stability. The explanation no doubt lies in the fact that traces of oxygen are scavenged by dianion 67 to form 1 (Scheme 10),

Scheme 10



whereas 1 generated directly from dione 40 is readily destroyed by oxygen.

In basic d_6-DMSO dione 49 exchanged all alpha hydrogens rapidly and completely giving a spectrum (Figure 5) with hfsc's of $a^H = 0.448$ (2H), $a^D = 0.925$ (2D), and 0.842 (2D) G, assigned to semidione 68. Brief exposure of 68 to oxygen



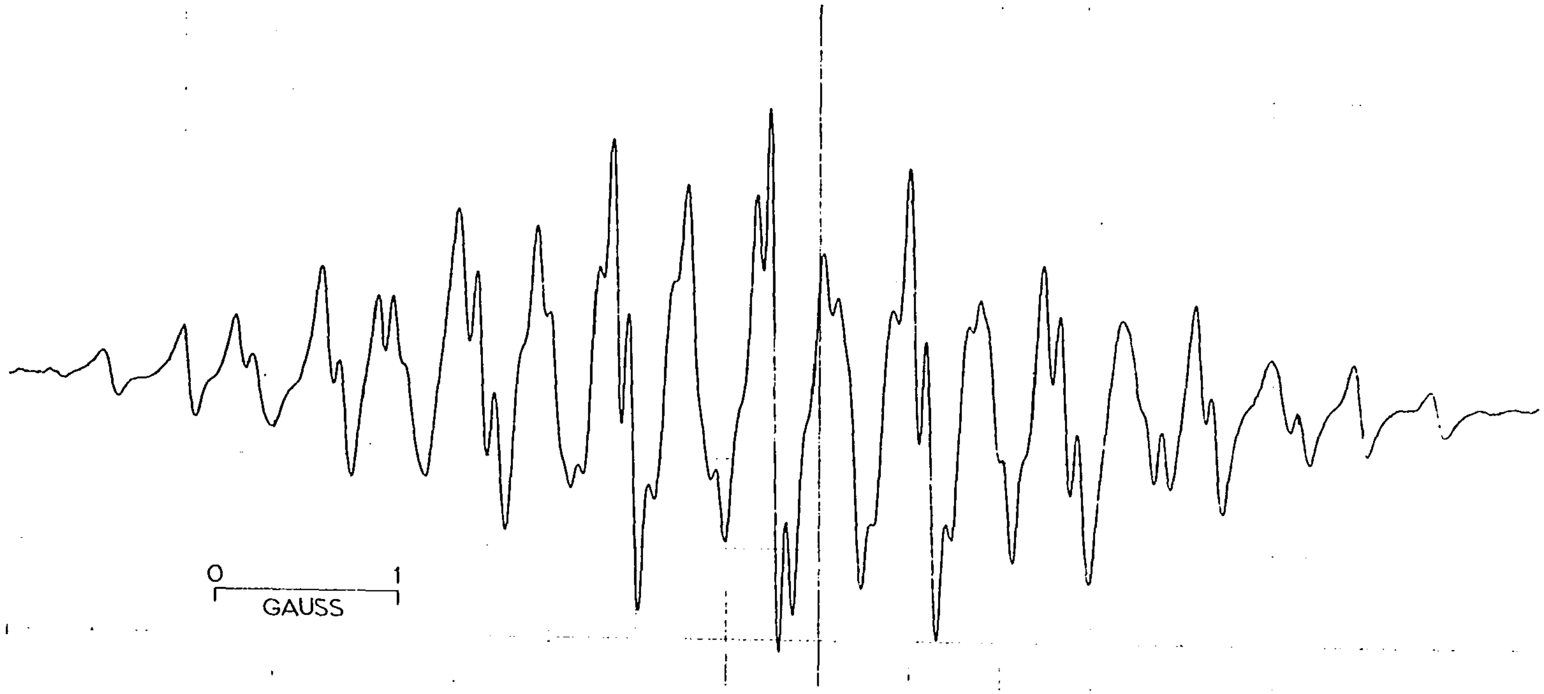
68

69

gave an esr spectrum assigned to semiquinone 69 (Figure 6). The presence of another radical (which increased when large quantities of oxygen were added) made solution of the spectrum difficult; however, the gross features are in very good agreement with a spectrum calculation substituting the appropriate values for deuterium for the hfsc's of semidione 62, $a^H = 1.83$ (2H), $a^D = 0.415$ (2D), and 0.305 (2D) G (Figure 6, bottom).

Chemical (B^-, DMSO) or electrolytic reduction of diones 41a and 41b gave semidiones 70a (Figure 7) and 70b (Figure 8), respectively (Table 3). Dione 41a gave semidione 70c (Figure 9, Table 3) in basic d_6-DMSO allowing assignment of $a^H = 4.68$ gauss to the bridgehead hydrogen.

Figure 5. The first derivative esr spectrum (top) obtained from bicyclo[4.2.0]octa-7-ene-2,5-dione (49) in d_6-DMSO; calculated spectrum (bottom) for Lorentzian line width 0.115 gauss with splitting constants from text.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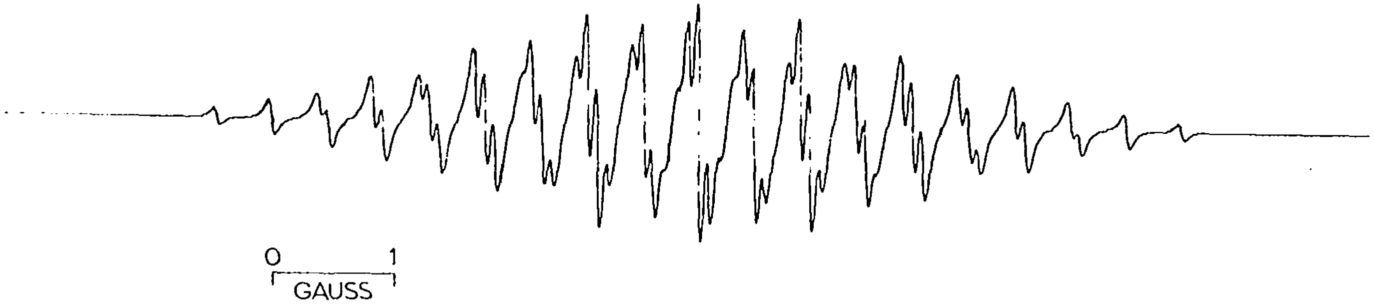
1
GAUSS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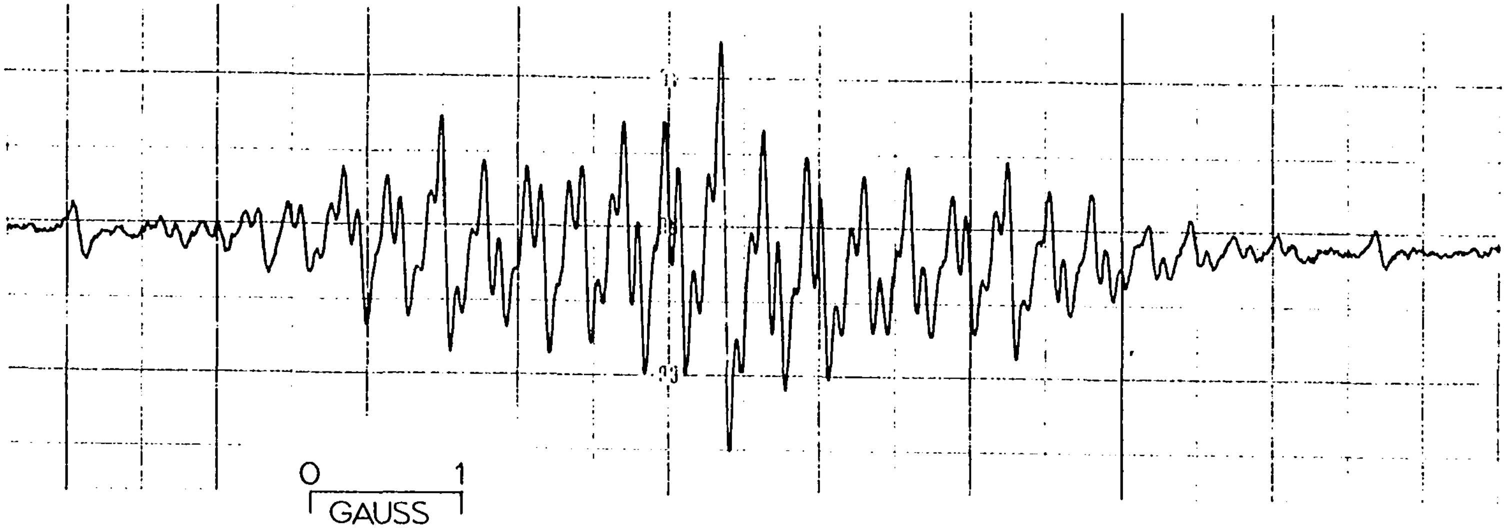
1
GAUSS

Figure 6. The first derivative esr spectrum (top) of semidione 69; calculated spectrum (bottom) for Lorentzian line width 0.100 gauss with splitting constants from text.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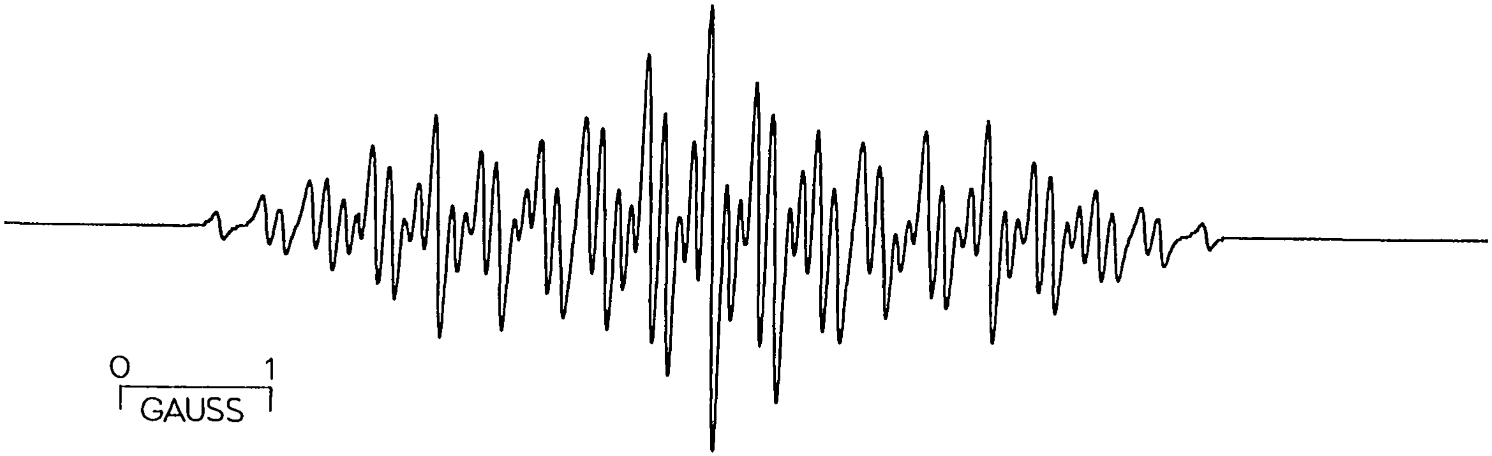
1
GAUSS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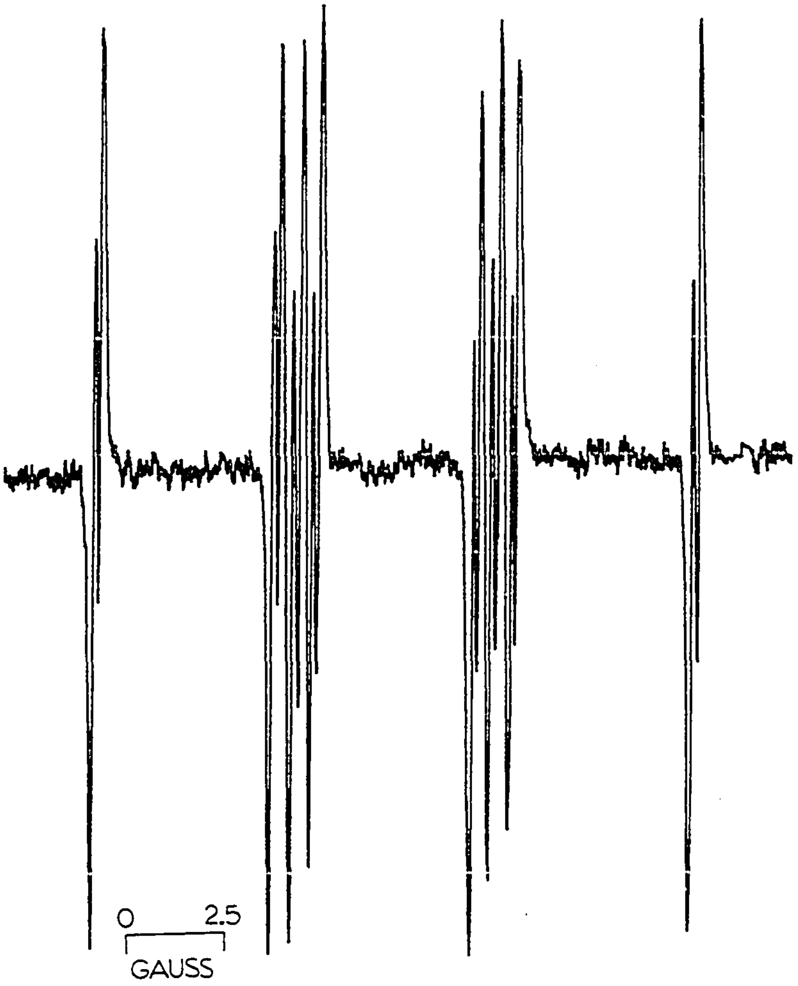
1
GAUSS

Figure 7. The first derivative esr spectrum (top) of 41a in basic DMSO; calculated spectrum (bottom) for Lorentzian line width 0.14 gauss with splitting constants from text.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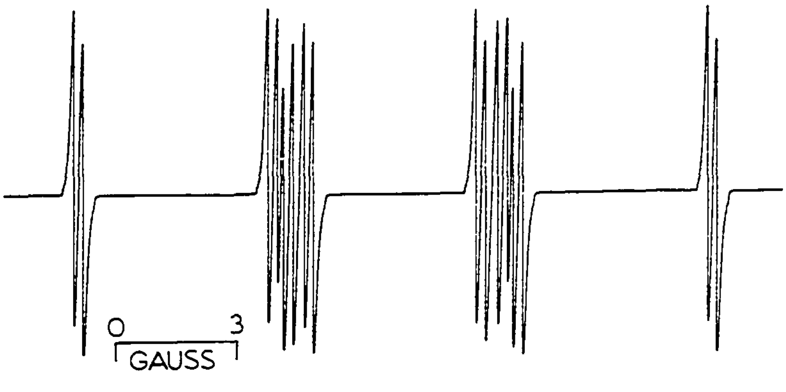
2.5
GAUSS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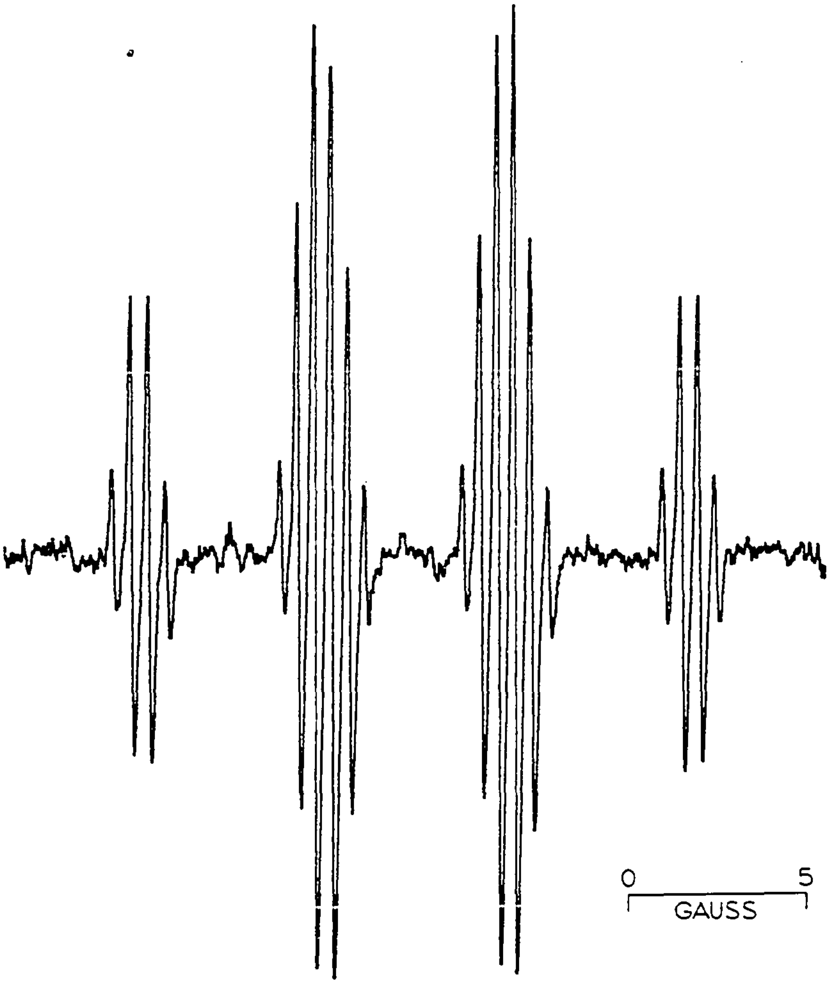
3
GAUSS

Figure 8. The first derivative esr spectrum (top) obtained from 41b in basic DMSO; calculated spectrum (bottom) for Lorentzian line width 0.15 gauss with splitting constants from text.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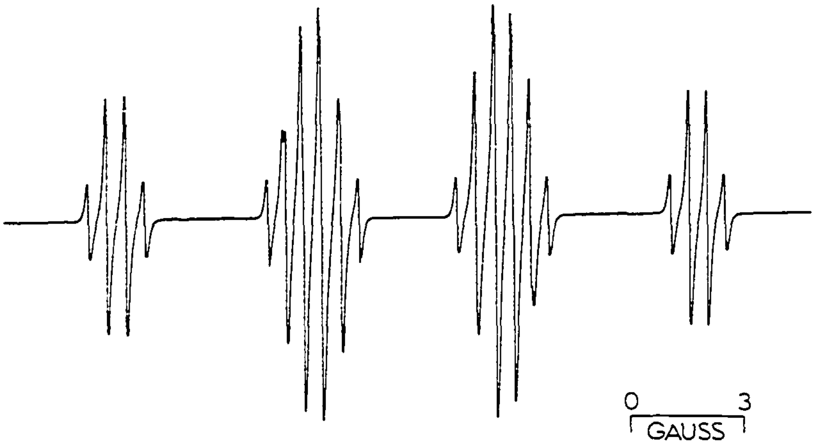
GAUSS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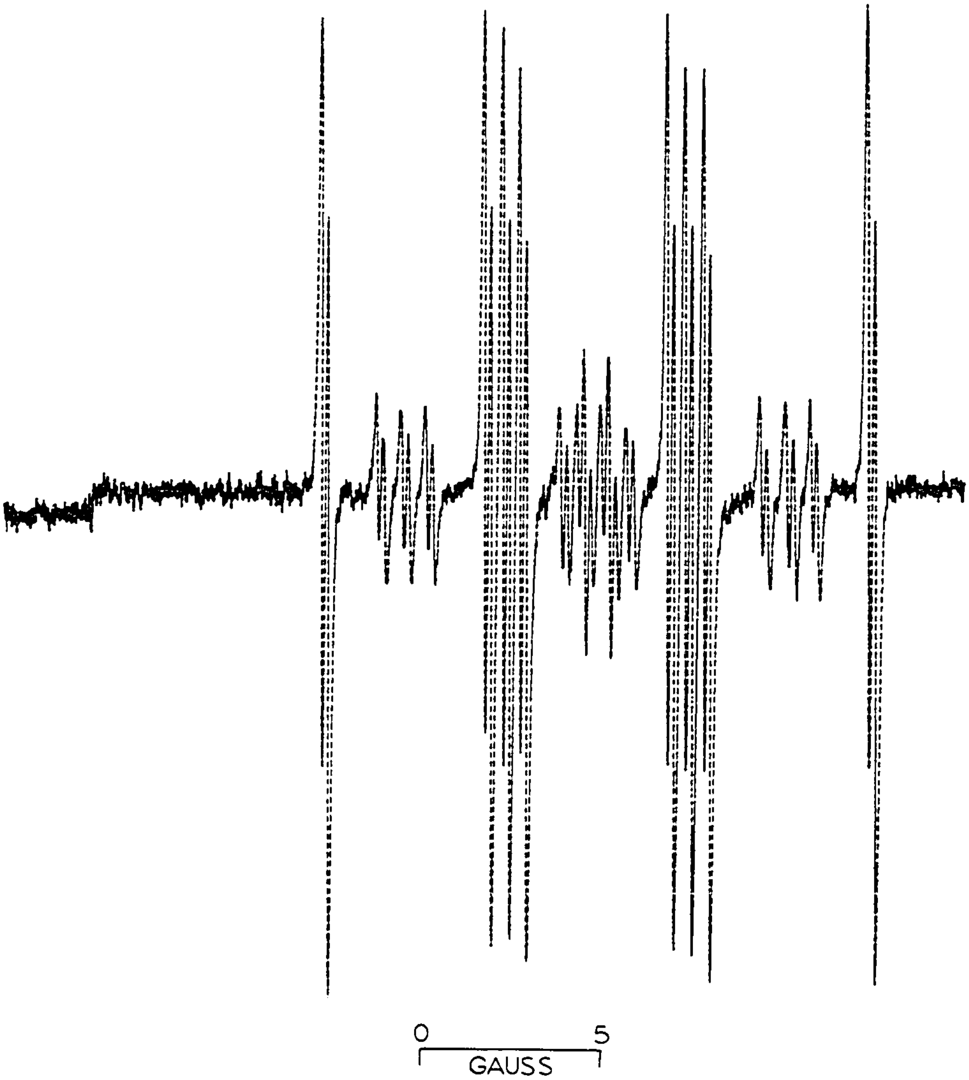
GAUSS

Figure 9. The first derivative esr spectrum (top) of 41a obtained in basic d_6-DMSO; calculated spectrum (bottom) of semidione 70c for Lorentzian line width 0.17 gauss with splitting constants from text.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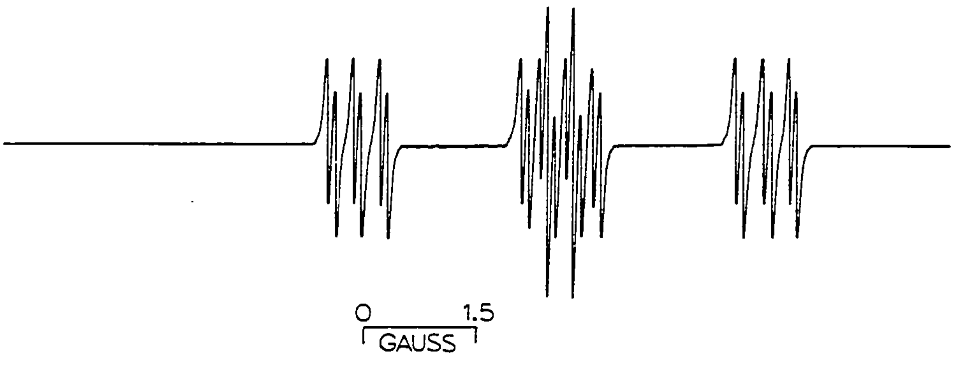
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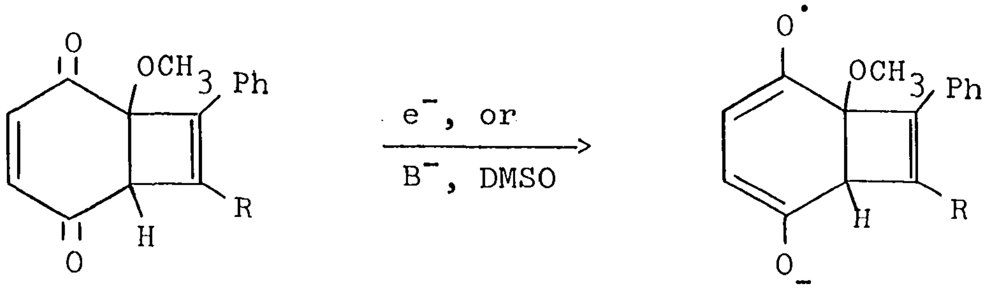
1.5
GAUSS

Table 3. Hyperfine splitting constants of semidiones <u>70a-c</u> generated from diones <u>41a-b</u>



<u>41</u>　　　　<u>70</u>

<u>41a</u>, R = H

<u>41b</u>, R = CH_3

<u>70a</u>, R = H, a^H = 5.58 (1H), 5.05 (1H), 4.68 (1H), 0.23 (1H) G

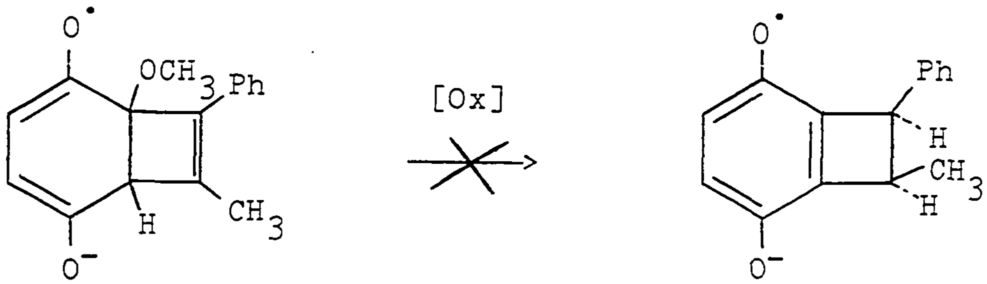
<u>70b</u>, R = CH_3, a^H = 5.65 (1H), 5.10 (1H), 4.70 (1H), $a^H_{CH_3}$ = 0.49 (3H) G

<u>70c</u>, R = H, a^H = 5.62 (1H), 5.12 (1H), 0.21 (1H), a^D = 0.70 (1D) G

Exchange of the bridgehead hydrogen is slow as evidenced by the signal shown in Figure 9. After approximately one-half hour the ratio of deuterated to nondeuterated semidione is about 1:5.

Irradiation at 2537Å through the fused silica esr cell window of a solution of 70b directly in the esr cavity was attended by a fading of the signal which would return, somewhat diminished in intensity, upon cessation of irradiation.

Addition of oxygen to a solution of semidione 70b destroyed its signal and a new signal, $a^H = 2.14$ (2H), and 0.82 (2H) G appeared. The hfsc of 0.82 gauss is certainly too small for the hydrogens on the ethano bridge of semidione 71. It was noted, however, that a very old (over 3 years) sample of dione 41b which did not give the expected signal of 70b gave, after addition of oxygen, the same signal described above. Thus, this signal was more than likely due to an unidentified impurity. It appears that semidione 70b is not oxidized to its corresponding semiquinone.

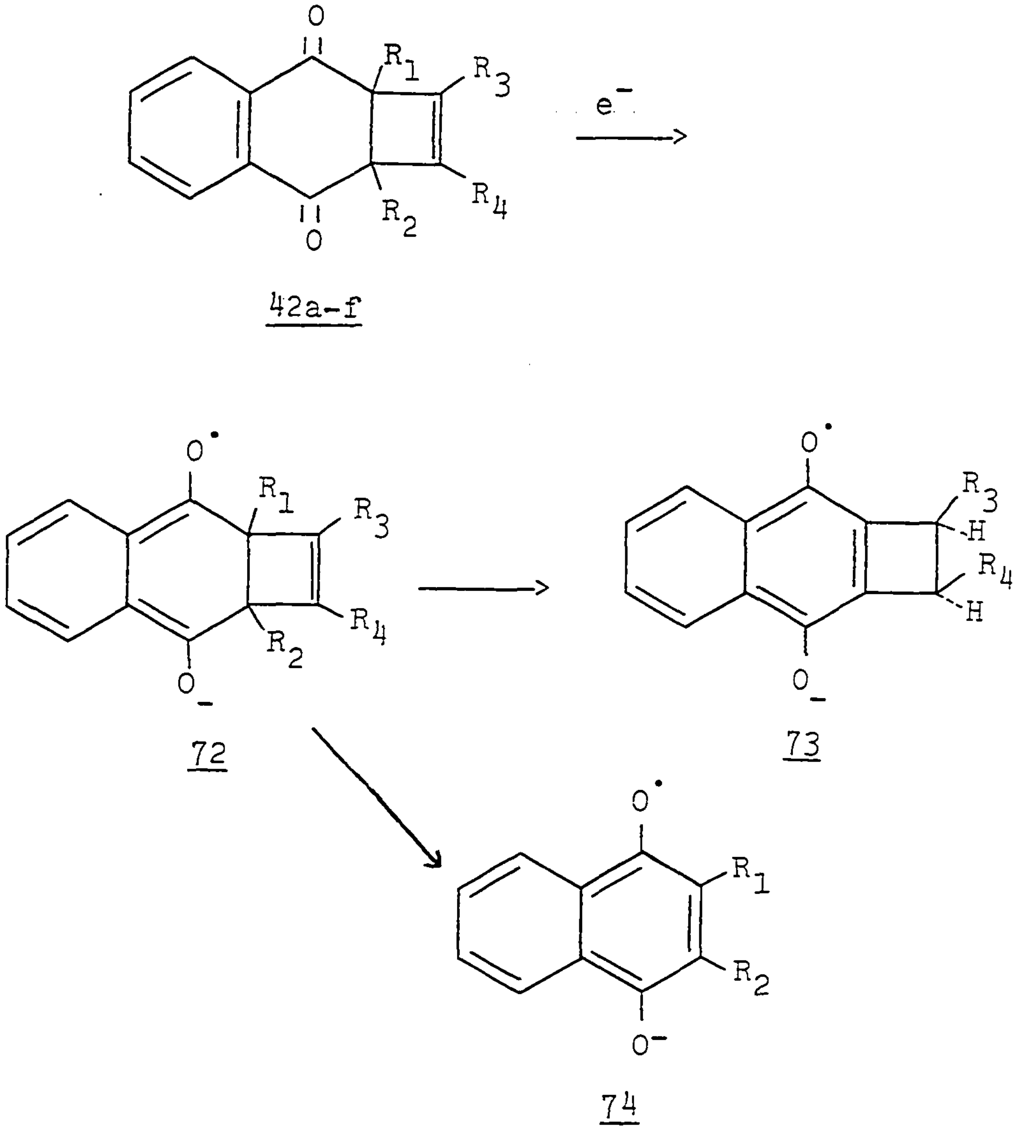


70b

71

Electrolytic reduction of the tricyclo[6.4.0.0^{3,6}]dodeca-4,8,10,12-tetraene-2,7-diones (42a-f) was found to be much more efficient than chemical reduction with potassium *t*-butoxide in DMSO. The reduction of diones 42a-f followed the general outline shown in Scheme 11, although not all of the radicals were observed for each dione (*vide infra*).

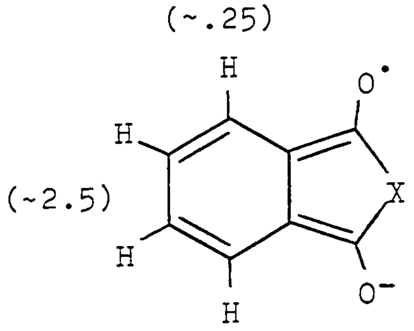
Scheme 11



The observed hfsc's for the radicals formed from 42a-f are given in Table 4.

The assignment of general structure 72 for the hfsc's listed in that column in Table 4 is supported by the reported hfsc's of a number of similar semidiones, 75 (75).

X = O, S, NH, CH_2, $CHCH_3$



75

The semidiones 72a,d,f were somewhat capricious in that they could not be routinely generated and had only transient existence. They were appreciably more stable in acetonitrile than in dimethylformamide.

Semidiones 73a-d were the final reduction products seen from 42a-d whether or not semidiones 72a-d were seen. The assignment of structure 73 to the observed hfsc's is on firm ground since semiquinone 73a has been generated from naphthoquinone 76 and the reported (73) splitting constants, a^H = 2.92 (4H), 0.75 (2H), and 0.44 (2H) G, are in excellent agreement with those shown in Table 4.

Table 4. Hyperfine splitting constants of radicals generated from diones 42a-f[a,b]

	42				72	73	74
	R_1	R_2	R_3	R_4			
a	H	H	Ph	Ph	a^H = 2.33 (2H), 6.02 (2H)[c]	a^H = 2.70 (2H), 0.63 (2H), 0.33 (2H)[c]	-
b	OCH_3	H	Ph	Ph	-	a^H = 2.73 (2H), 0.70 (2H), 0.35 (2H)[c]	-
c	OCH_3	H	Ph	H	-	a^H = 2.99 (1H), 2.78 (1H), 2.65 (1H), 0.72 (2H), 0.36 (2H)[d]	-

---

[a] Splitting constants in gauss.

[b] Dash (-) indicates not observed.

[c] Figure 10.

[d] Figure 11.

Table 4. (Continued)

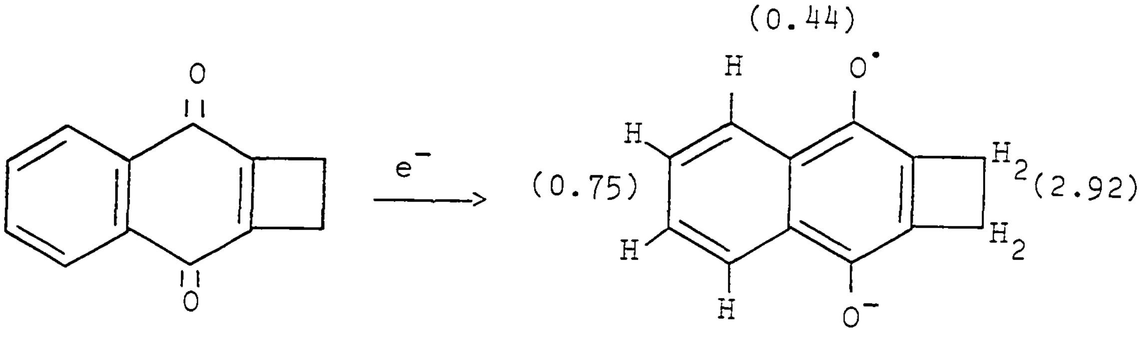
	<u>42</u>				<u>72</u>	<u>73</u>	<u>74</u>
	R_1	R_2	R_3	R_4			
<u>d</u>	H	H	CH_3	CH_3	a^H = 5.43 (2H), 2.48 (2H), 0.21 (6 or 8H)[e]	a^H = 2.25 (2H), 0.52 (2H), 0.26 (2H), 0.13 (6H)[f]	-
<u>e</u>	CH_3	CH_3	CH_3	CH_3	-	-	a^H = 2.50 (6H), 0.72 (2H), 0.36 (2H)[g]
<u>f</u>	CH_3	CH_3	Ph	H	a^H = 2.20 (2H)(transient)	-	a^H = 2.48 (6H), 0.71 (2H), 0.35 (2H)[g]

---

[e] Figure 12.

[f] Figure 13.

[g] Figure 14.



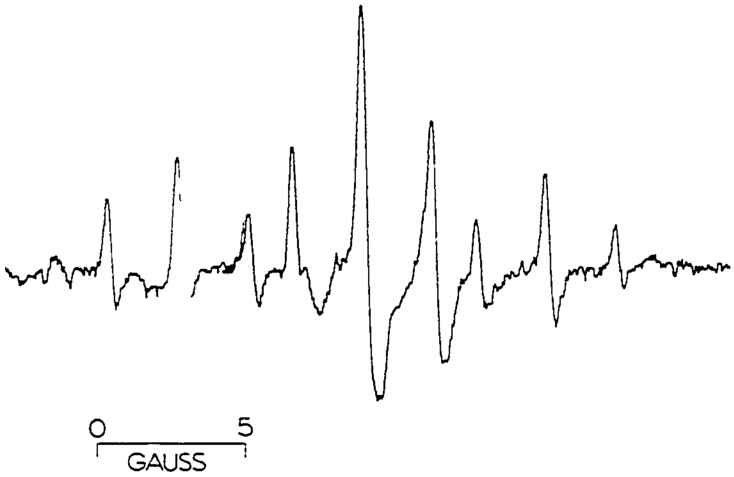
76 73a

Diones 42a,b both gave the same semiquinone 73a (Figure 10). This result can be rationalized by the mechanism shown in Scheme 12 which has been shown to have a photochemical counterpart (76).

The transformation of the intermediate semidiones 72a-d (whether or not detected) to semiquinones 73a-d must be a facile process since it was found to occur even when deoxygenation was done by the freeze-pump-thaw technique. This is in contrast to the oxidation of semidione 1 to semiquinone 62 which is effected only by the addition of significant amounts of oxygen to the esr cell.

A concerted mechanism in which semidiones 72 are converted to semiquinones 73 by oxygen-mitigated hydrogen-transfer seems unlikely since electrolytic reduction of 42b in d_6-DMSO gave an esr signal, $a^H = 0.70$ (2H), 0.35 (2H), and $a^D = 0.41$ (2D) G, (Figure 15), which was assigned to

Figure 10. The first derivative esr spectrum (top) of semidione 72a; the first derivative esr spectrum (middle) of semiquinone 73a; the calculated spectrum (bottom) of semiquinone 73a for Lorentzian line width 0.25 gauss with splitting constants from Table 4.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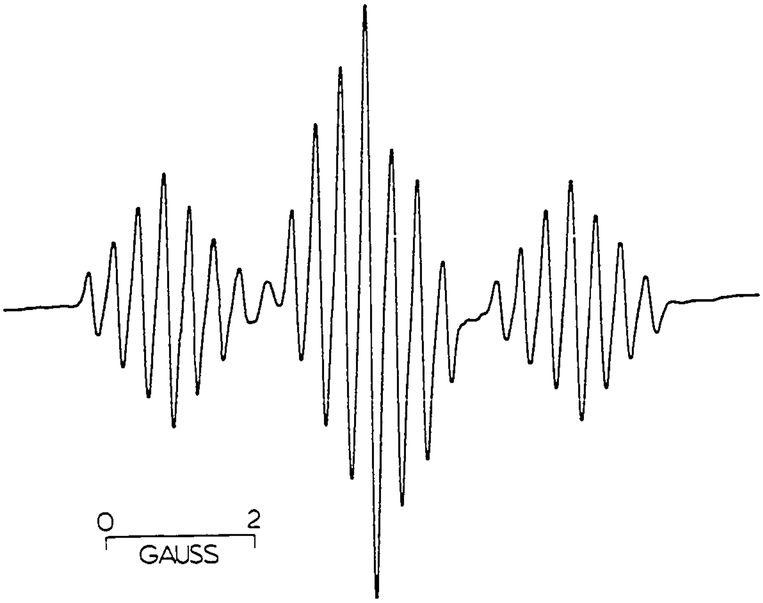
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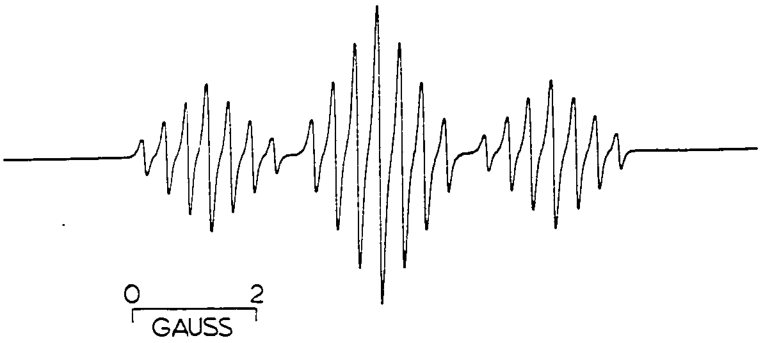
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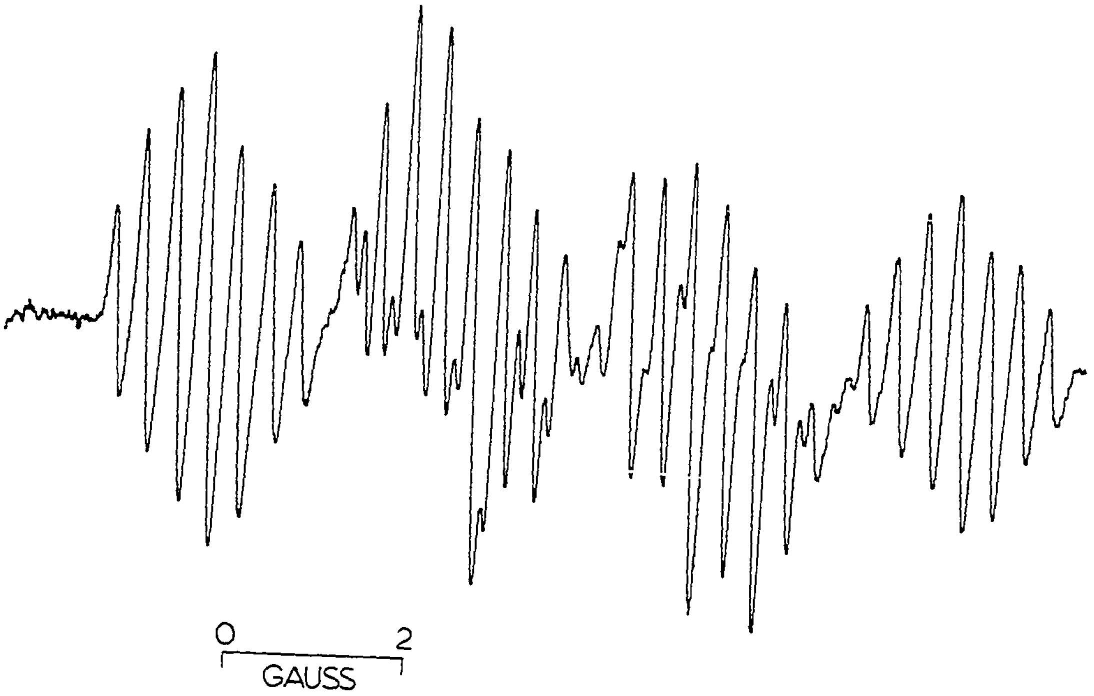
Figure 11. The first derivative esr spectrum (top) of semiquinone 73c; calculated spectrum (bottom) for Lorentzian line width 0.19 gauss with splitting constants from Table 4.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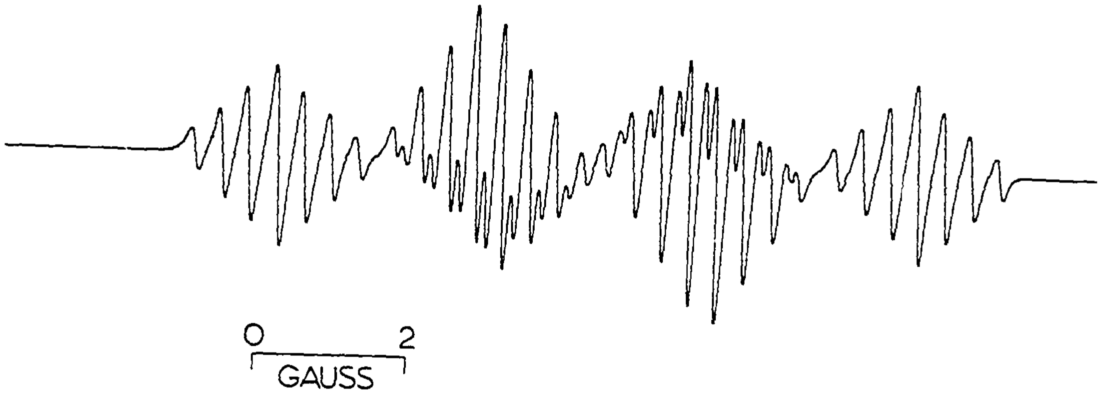
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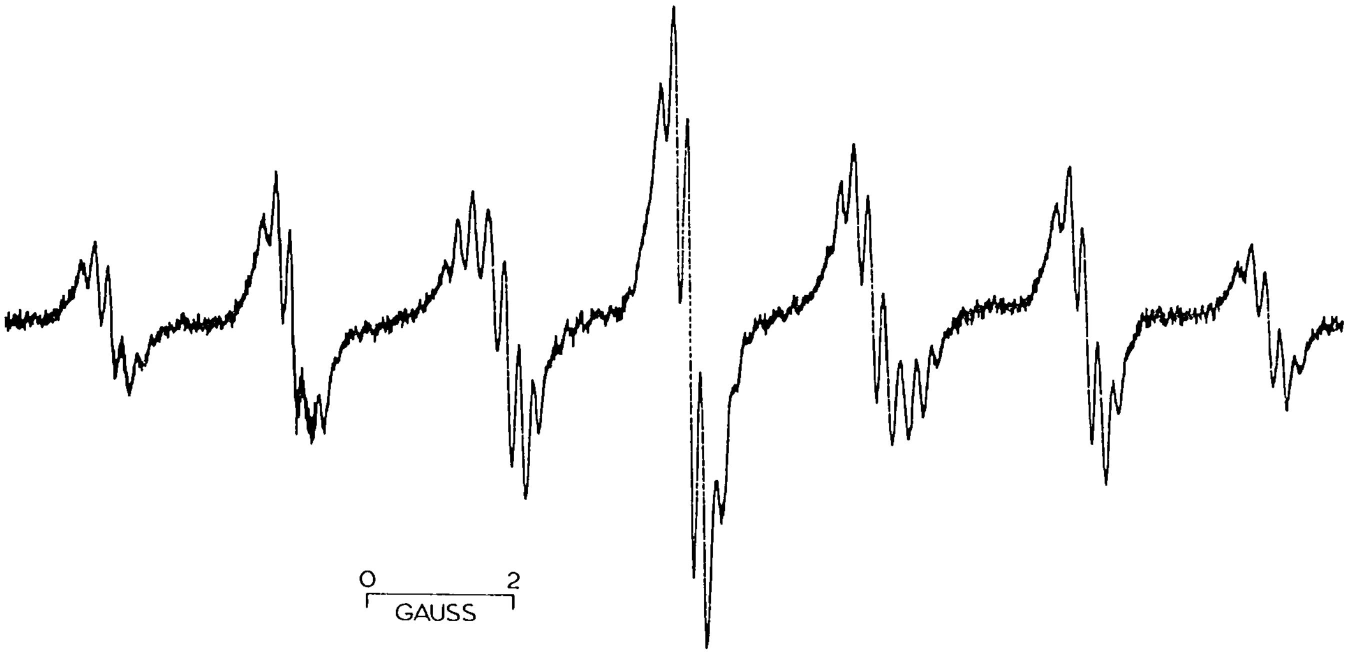
Figure 12. The first derivative esr spectrum (top) of semidione 72d; calculated spectrum (bottom) for Lorentzian line width 0.25 gauss with splitting constants from Table 4.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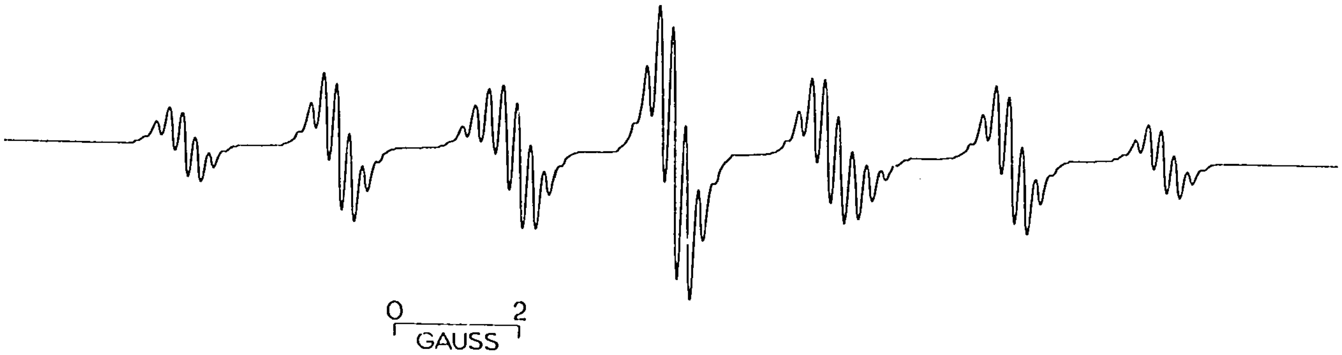
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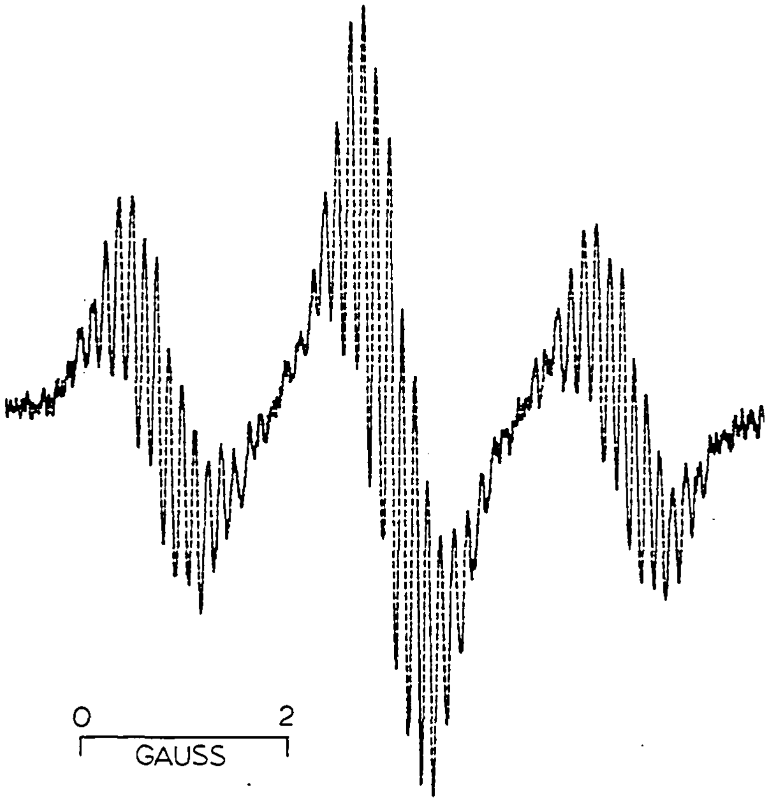
Figure 13. The first derivative esr spectrum (top) of semiquinone 73d; calculated spectrum (bottom) for Lorentzian line width 0.90 gauss with splitting constants from Table 4.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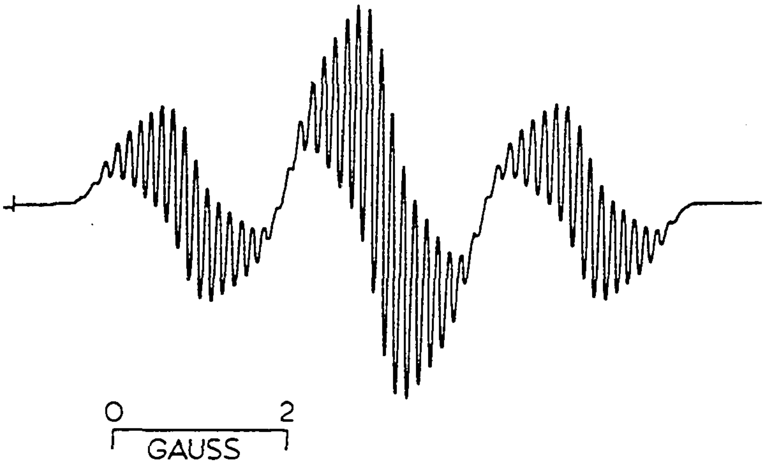
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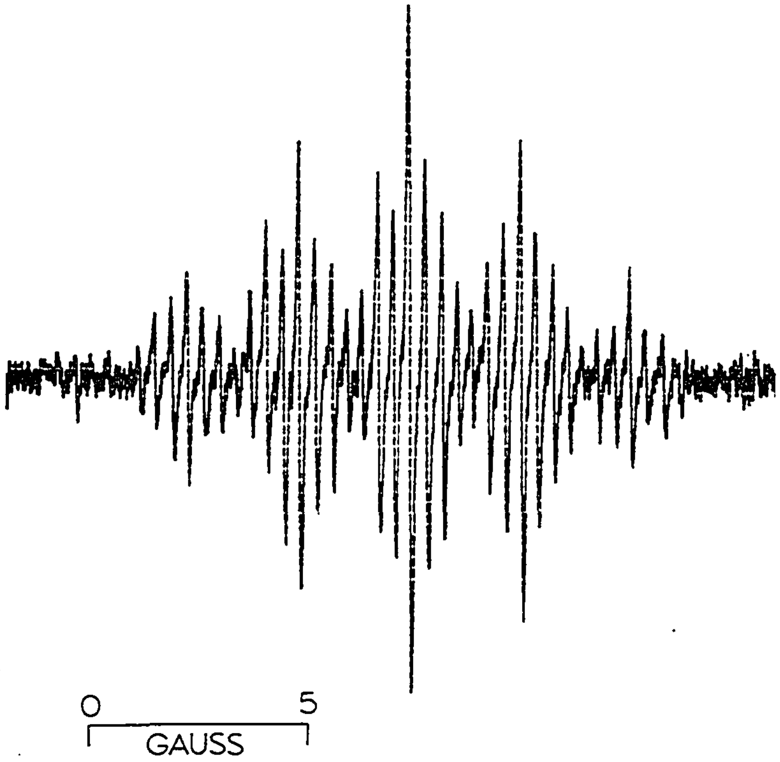
Figure 14. The first derivative esr spectrum (top) of semiquinone <u>74e</u>; calculated spectrum (bottom) for Lorentzian line width 0.20 gauss with splitting constants from Table 4.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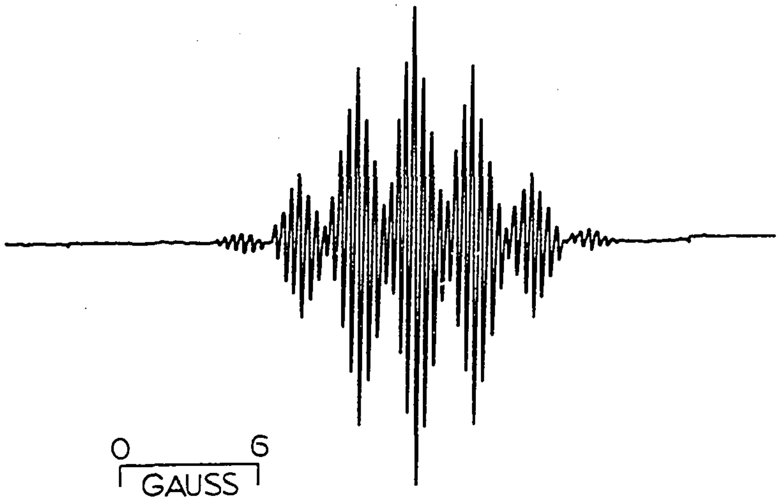
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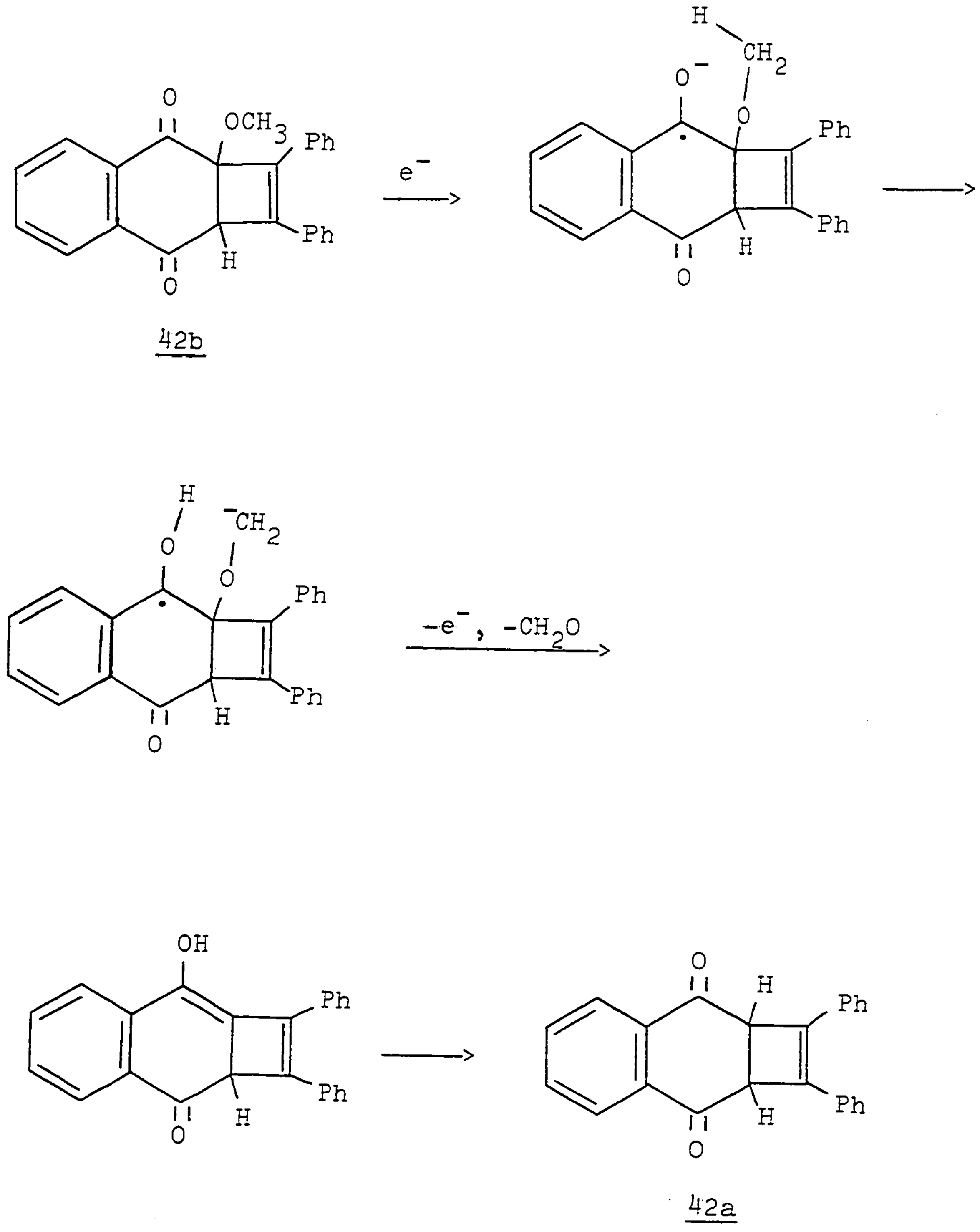
Scheme 12


O
OCH3
Ph
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H
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42b
e⁻
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⁻CH2
O
O
Ph
Ph
H
O
−e⁻, −CH2O
OH
Ph
Ph
H
O
O
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Ph
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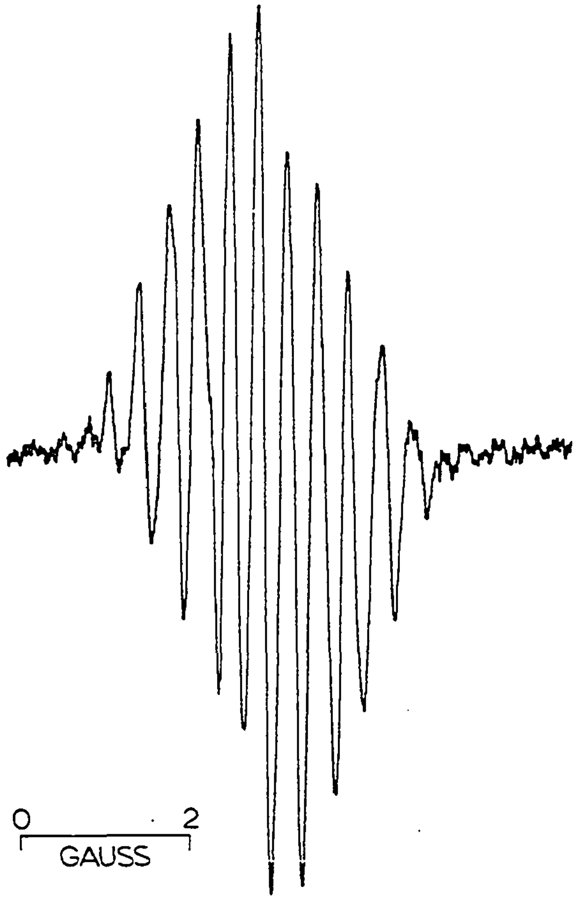
42a

Figure 15. The first derivative esr spectrum (top) of semiquinone <u>77</u>; calculated spectrum (bottom) for Lorentzian line width 0.14 gauss with splitting constants from text.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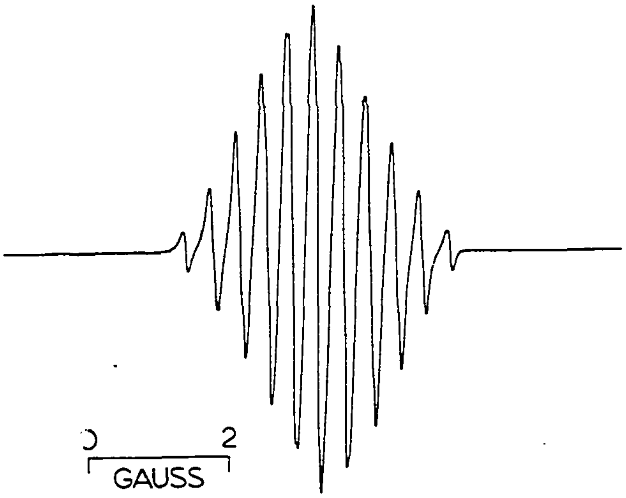
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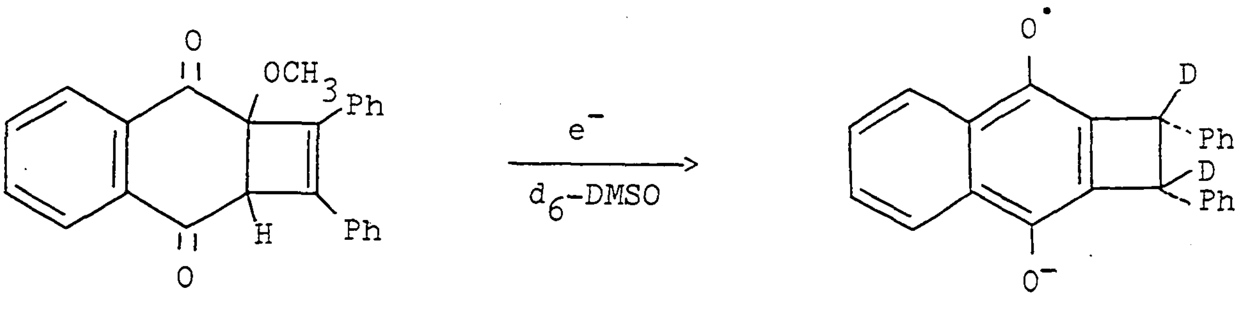
semiquinone 77, the dideuterio analogue of 72b. If the

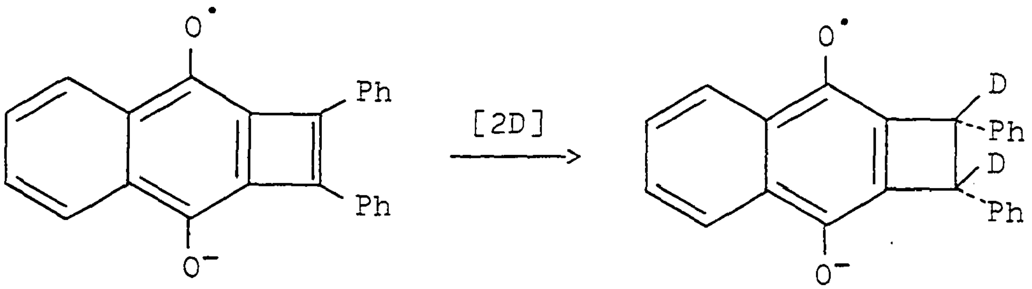


42b

77

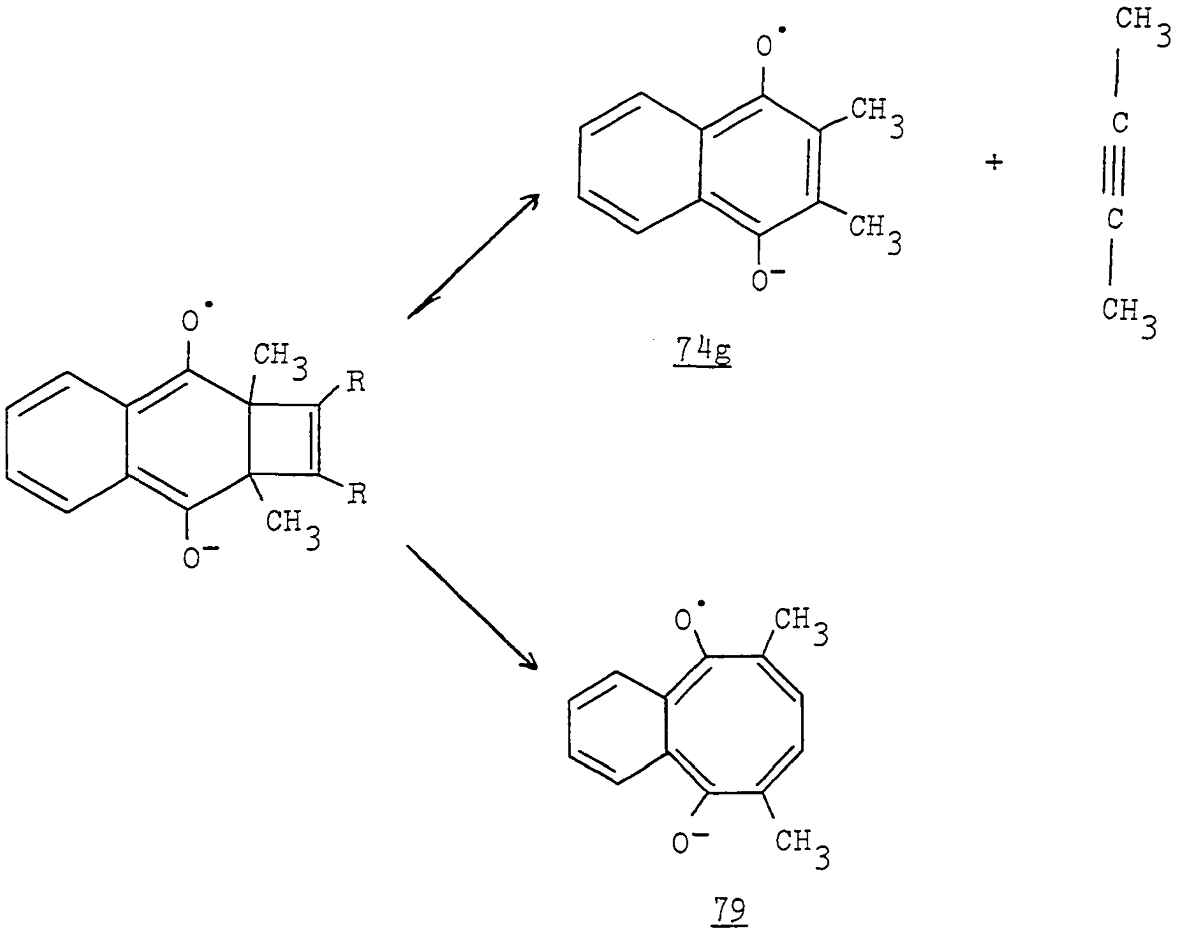
mechanism of methoxide elimination is indeed that shown in Scheme 12 and the transfer of the bridgehead protons is concerted, only one deuterium atom should be transferred to the ethano bridge in 77. Of course, exchange of the bridgehead hydrogens before isomerization would also explain the transfer of two deuterium atoms and, indeed, Breslow and coworkers have shown (76) that in very basic solutions exchange and even alkylation at the bridgehead is quite facile. The analogy to the electrolytic process is, however, difficult to assess.

A more likely intermediate is the cyclobutadiene-semiquinone 78 which would rapidly pick up deuterium from solvent. Breslow and coworkers (76) have obtained polarographic data demonstrating the existence of 78. Other examples of strained semidiones taking on two hydrogen atoms to relieve strain have been reported (20, 77).



78 77

Substitution of methyl groups at the bridgehead position as in 42e and f should prevent oxidation to intermediates like 78. Indeed, it was observed that electrolytic reduction of 42e or f did not form semiquinones 73. Rather, the final spectrum for both was identified as that of 2,3-dimethyl semiquinone (74g). It appears that fragmentation is a less energy demanding process than the valence isomerization to 79. At times during the electrolytic reduction of 42f a strong, stable signal was observed after the disappearance of the signal for 72f. This signal was easily analyzed for a^H = 6.54 (1H), 5.12 (1H), 1.39 (1H), 1.0 (1H), and 0.51 (1H) G, which in d_6-DMSO appeared to exchange the hydrogens of splitting constants 1.00 and 0.51 gauss for deuterium. The structure of this radical has not been assigned. More extensive reduction always led to formation of 2,3-dimethylnaphthosemiquinone (74g).



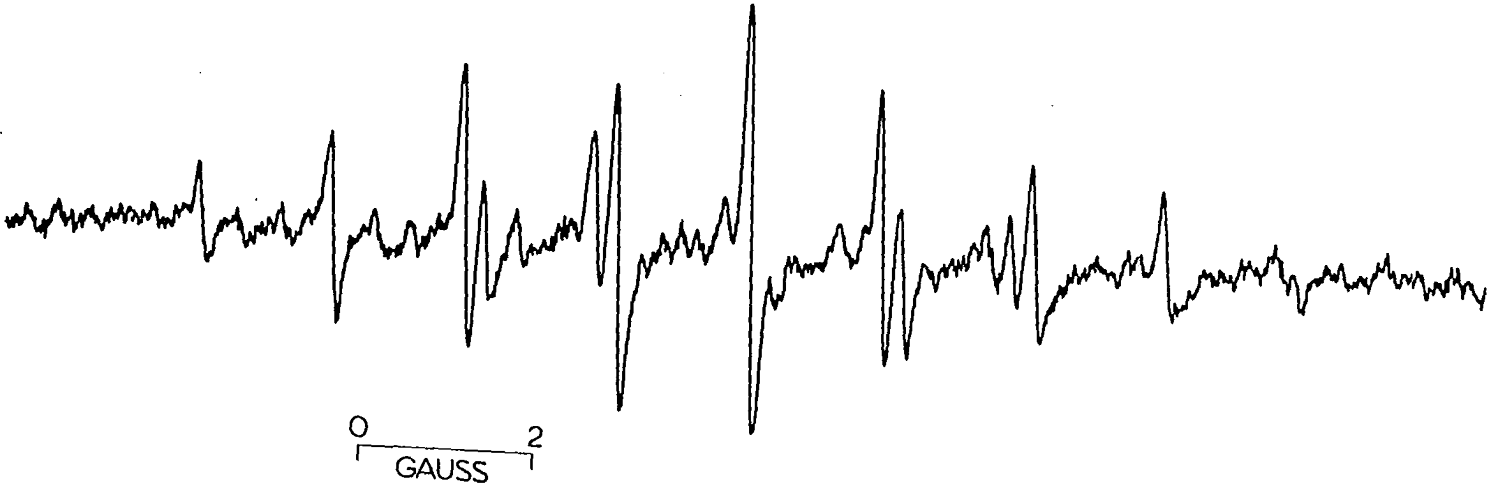
74g

79

An example wherein addition of an electron to a LUMO permits a 2+2 cycloaddition to become thermally reversible has been reported (78).

Another example of this phenomenon was observed for quinone photodimer 80. The initial signal observed upon electrolytic reduction of 81 was assigned to semidione 81, a^H = 3.29 (2H), and 1.53 (6H) G (Figure 16).

Figure 16. The first derivative esr spectrum (top) of semidione 81; calculated spectrum (bottom) for Lorentzian line width 0.18 gauss with splitting constants in text.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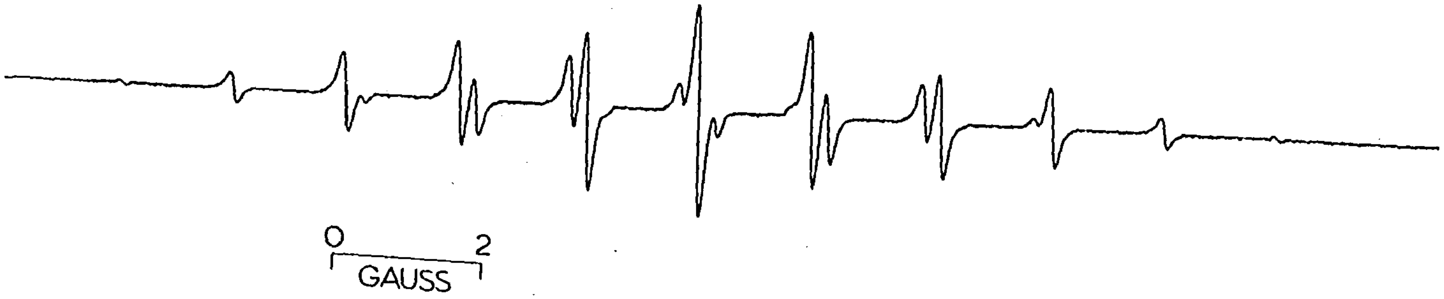
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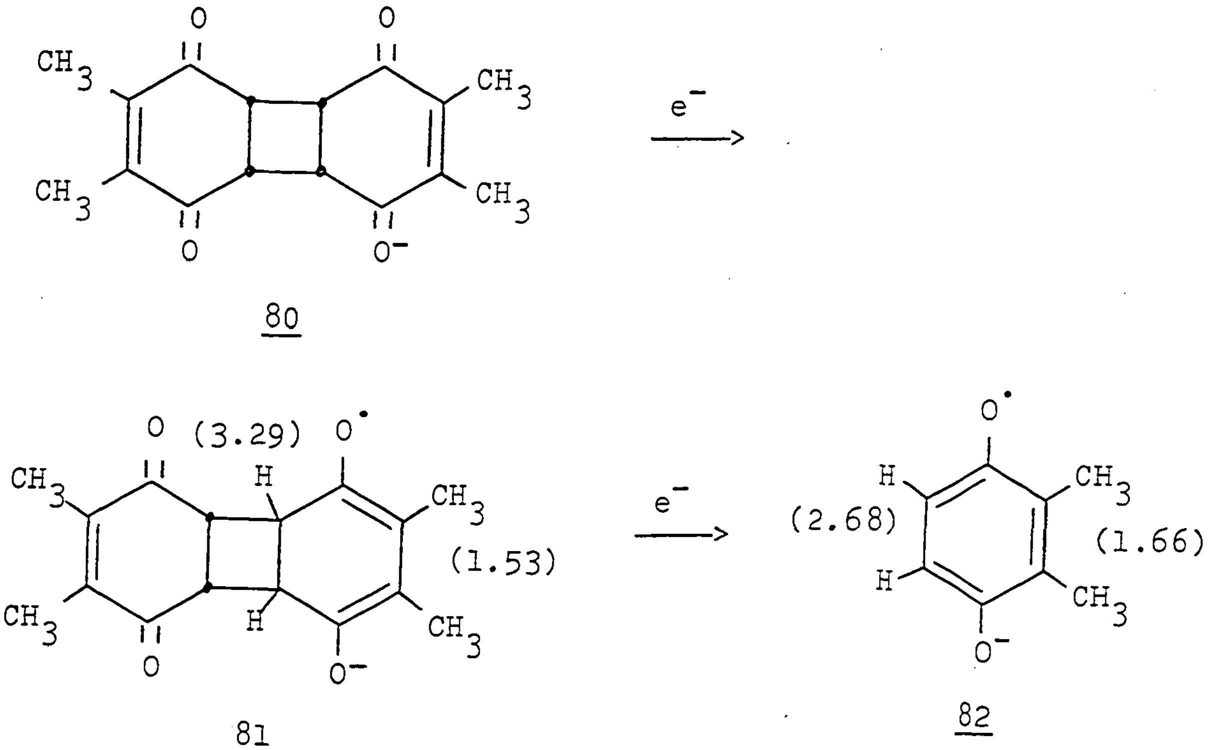


80

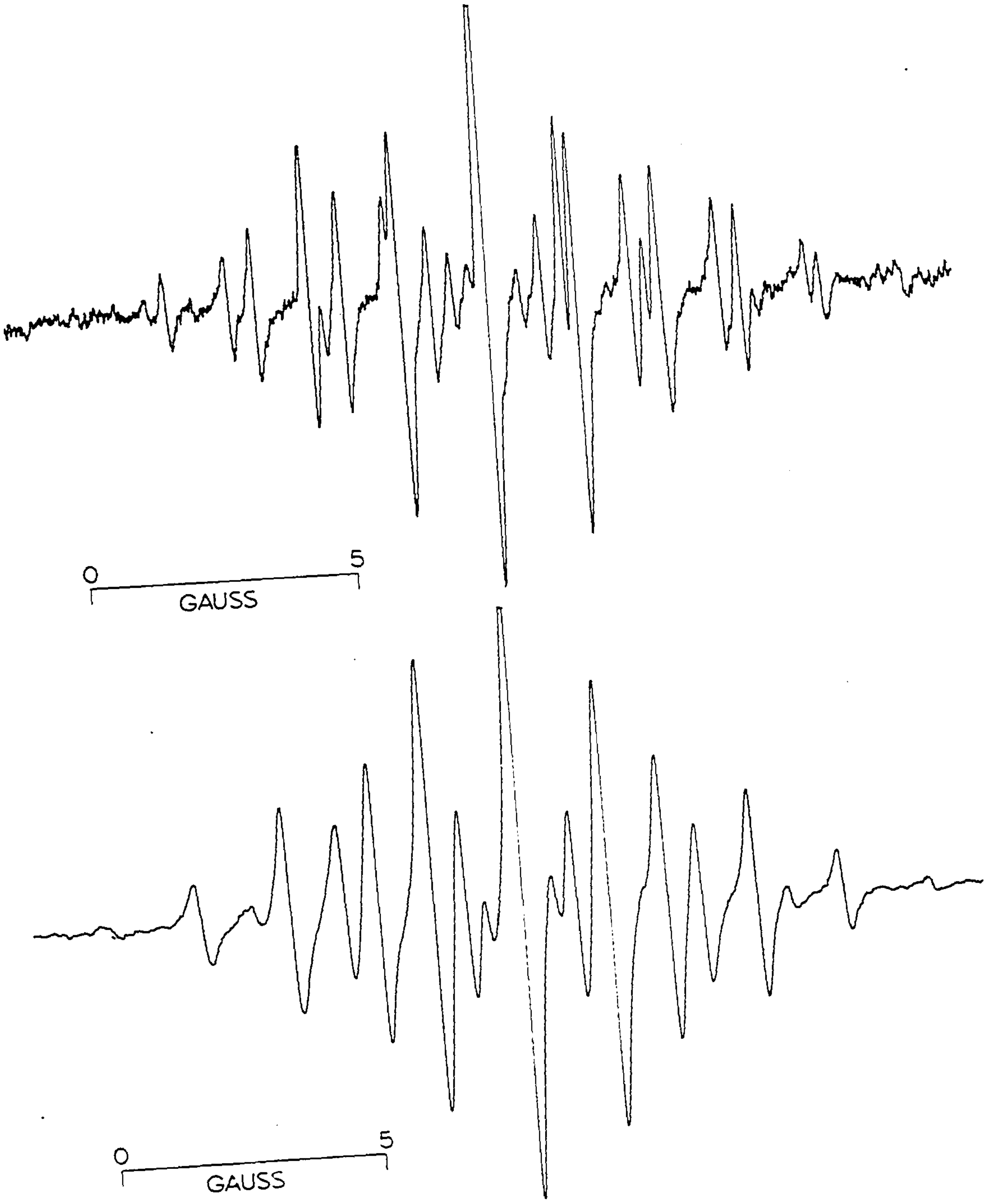
81

82

Raising the applied voltage resulted in the appearance of a new signal along with that of 81 which was found to be identical to that of 2,3-dimethylsemiquinone (82), a^H = 2.68 (2H), and 1.66 (6H) G. Figure 17 shows the esr spectrum of this mixture of radicals and also the spectrum of 82 itself for reference. The fact that greater reduction was required to fragment 81 may perhaps imply that fragmentation occurs *via* the dianion.

Treatment of 42d with potassium *t*-butoxide in DMSO gave a strong spectrum with hfsc's of a^H = 2.46 (1H), 1.52 (1H), and 0.62 (1H) G. The splitting constants are those of the

Figure 17. The first derivative esr spectrum (top) of radicals observed upon greater reduction of semidione 81; the first derivative esr spectrum (bottom) of 2,3-dimethylsemiquinone (82).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GAUSS
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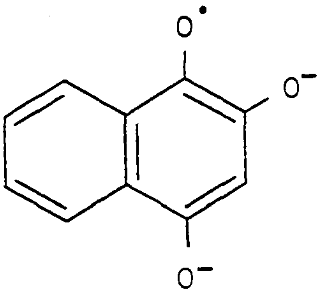
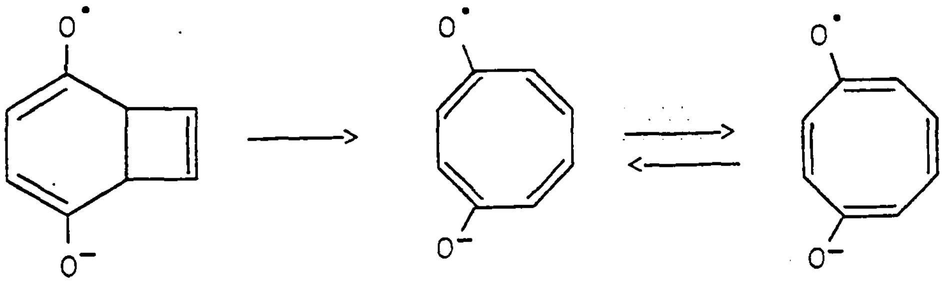
5
GAUSS

lawsone radical dianion (83) which is formed from a variety of precursors (22, and references therein).



83

All of the experiments reported in this section (with the possible exception of the photochemical conversion of 1 to 64) failed to give any evidence for the conversion of 1 to 2. However, the question of the irreversible conversion



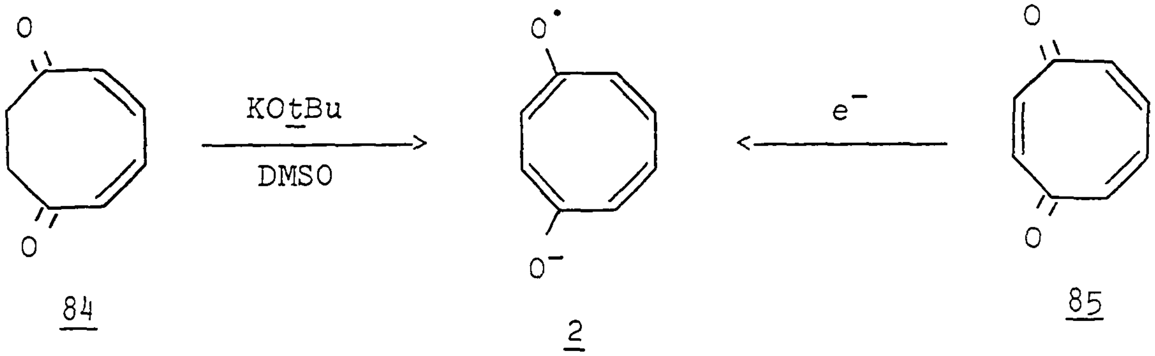
1

2

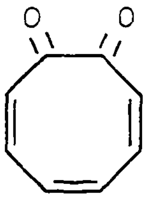
conversion of 2 to 1 (or the interconversion with an equilibrium greatly in favor of the bicyclic structure) remained unanswered. We thus turned our attention to the synthesis of possible precursors of 2 which would allow us to enter the potential energy surface at the monocyclic structure.

Synthesis and Purification of 2,4-Cyclooctadiene-1,6-dione and 2,5,7-Cyclooctatriene-1,4-dione

By analogy to the methods used to generate semidione 1, logical precursors to 5,7-cyclooctadiene-1,4-semidione (2) are 2,4-cyclooctadiene-1,6-dione (84) and 2,5,7-cyclooctatriene-1,4-dione (85).

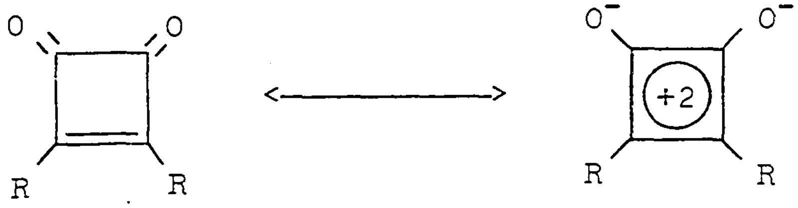


Triene-dione 85 and its isomer 86 (commonly referred to



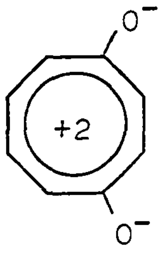
86

as cyclooctatetraene quinones) have been the object of considerable synthetic effort. It was proposed (79) that in analogy to the cyclobutenediones whose unusual stability is attributed to contributions from resonance structure 87 (80), diones 85 and 86 might possess some aromatic character as a

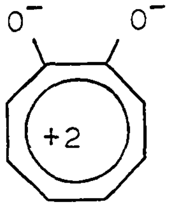


87

result of contributions from resonance forms 88 and 89.

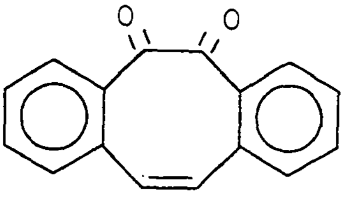


88



89

When one considers the increase in angle strain required for the achievement of planarity of eight-membered rings and the charge separation entailed in such forms as 88 and 89, the net stabilization due to aromaticity might be expected to be slight. Indeed, for the 1,2- and 1,4-cyclooctatetraene quinones reported at the time this work began (90 (79), 91 (81), 92 (81), and 93 (82)) no evidence existed to substantiate aromatic character.



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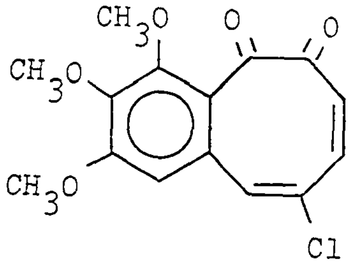

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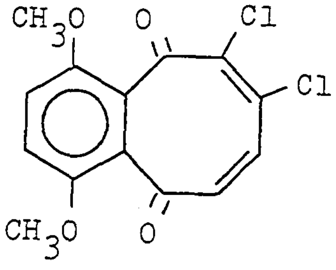

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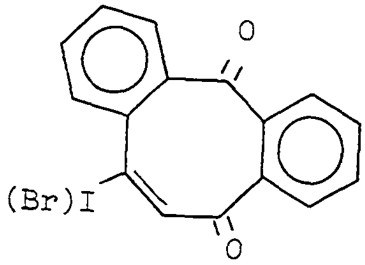


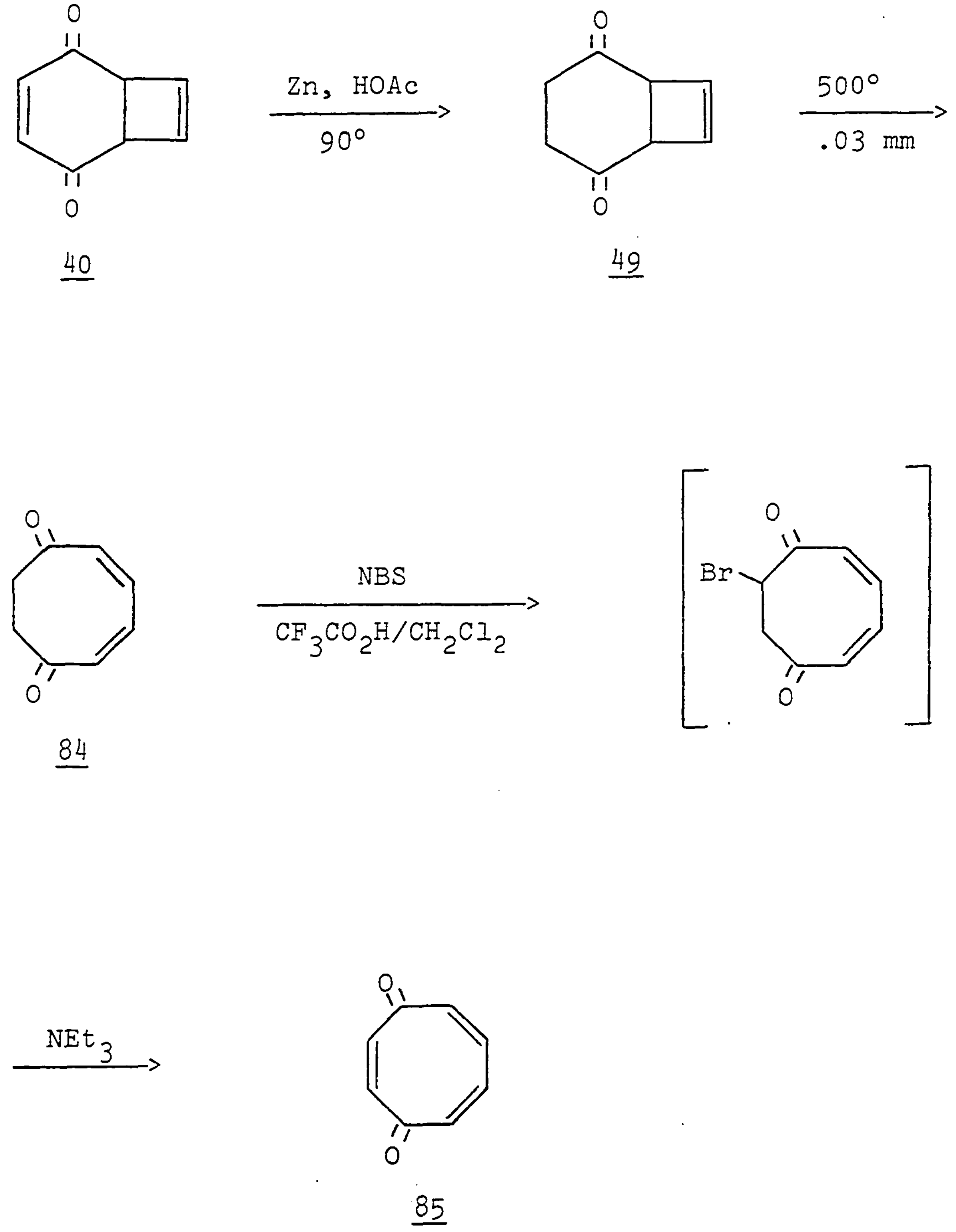
93

The cyclooctatriene-1,4-diones 92 and 93 were deemed unsuitable for this work since in either case valence isomerization of the corresponding semidione would more than likely be complicated by the fused aromatic rings.

The synthesis of both 84 and 85 was recently reported by Oda and coworkers (83) and is shown in Scheme 13. The reported physical data (pmr and ir spectra) indicate that triene-dione 85 possesses negligible aromatic character.

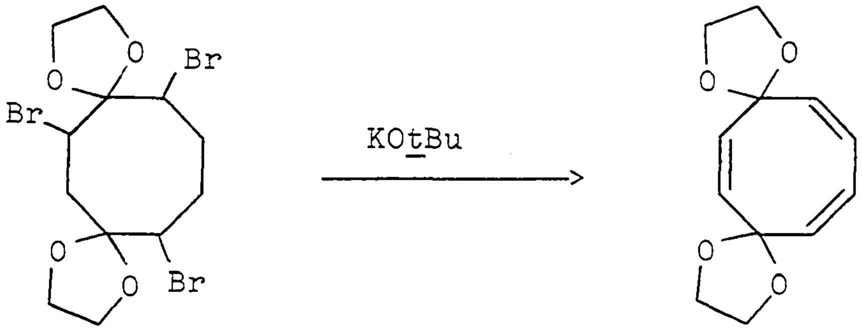
One can envision an alternate scheme in which 40 is pyrolyzed directly to 85. However, Kayama and coworkers

Scheme 13



(84) have demonstrated that pyrolysis of 40 gives tropone with no detectable amounts of 85.

Diene-dione 84 is reported to be unstable to base and dione 85 is unstable under acidic conditions or in protic solvents. A recent report (85) described the preparation of cyclooctatriene-1,4-dione bisethyleneketal (95) from the tribromide 94, but made no mention of the conversion of 95 to 85. Since removal of the ketal protecting group would require acidic conditions, these authors more than likely found that deketalization was accompanied by decomposition.



94 95

The sensitivity of compounds 84 and 85 hampered rigorous purification. Samples of diene-dione 84 obtained by pyrolysis of 40 were of approximately 85-90% purity by pmr. Attempted purification of 84 by preparative thin layer chromatography (silica gel and alumina) was accompanied by decomposition as evidenced by a great amount of streaking on the plate and poor recovery of purified material. Purification was also attempted by gas chromatography. Here, too, considerable decomposition was evident on a variety of columns. Molecular distillation, although causing no visible changes in the pmr spectrum, was found to be the most convenient method of purification for diene-dione 84. Without some purification (molecular distillation being the most convenient) samples of 84 did not give resolvable esr spectra (*vide infra*). Estimated purity of the samples of 84 used for esr experiments was 95%.

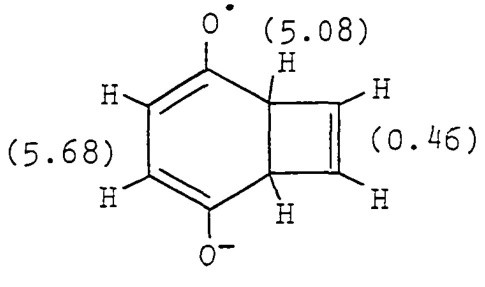
Triene-dione 85 was not satisfactorily purified by column chromatography. However, it was found that 85 could be purified by gas chromatography resulting in material estimated at 98% purity or better.

Attempts to Generate 5,7-Cyclooctadiene-1,4-semidione

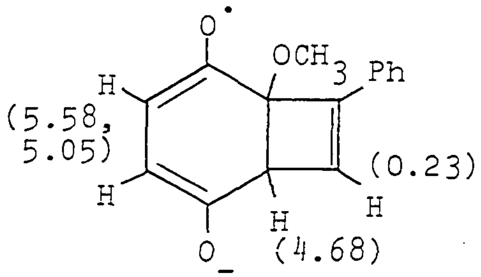
Samples of 2,5,7-cyclooctatriene-1,4-dione (85) dissolved in DMF or DMSO discolored rapidly, changing from light yellow to brown in a matter of minutes. Solutions of 85 in acetonitrile retained its characteristic light yellow color.

Electrolytic reduction of 85 in acetonitrile at a mercury pool cathode or in tetrahydrofuran at -40° at a platinum electrode gave very weak, unresolvable esr signals. Treatment with potassium *t*-butoxide again gave a weak unresolvable signal which upon addition of oxygen disappeared and was replaced by the strong signal of p-benzosemiquinone, a^H = 2.41 (4H) G. Thus, attempts to generate 5,7-cyclooctadiene-1,4-semidione (2) from its most immediate precursor, 2,5,7-cyclooctatriene-1,4-dione (85), were unsuccessful.

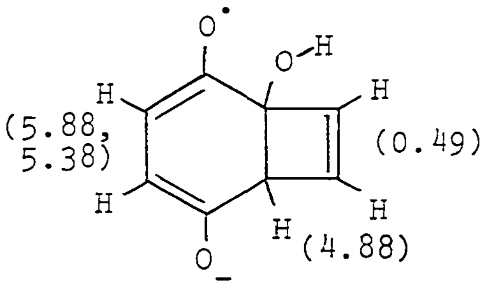
However, treatment of freeze-pump-thaw degassed DMSO solutions of diene-dione 84 with potassium t-butoxide gave an intense cherry red solution which changed to emerald green in the time it took to tune the spectrometer. The fairly strong signal recorded is shown in Figure 18. This signal was quite stable and showed no decrease in intensity after two hours. The solution of this spectrum gave hfsc's of a^H = 5.88 (1H), 5.38 (1H), 4.88 (1H), and 0.49 (2H) G. The splitting constants are consistent with a bicyclic structure and, in fact, comparison with the hfsc's of semidiones 1 and 70a leads us to assign the signal to semidione 96 (or a very similar structure).



1



70a



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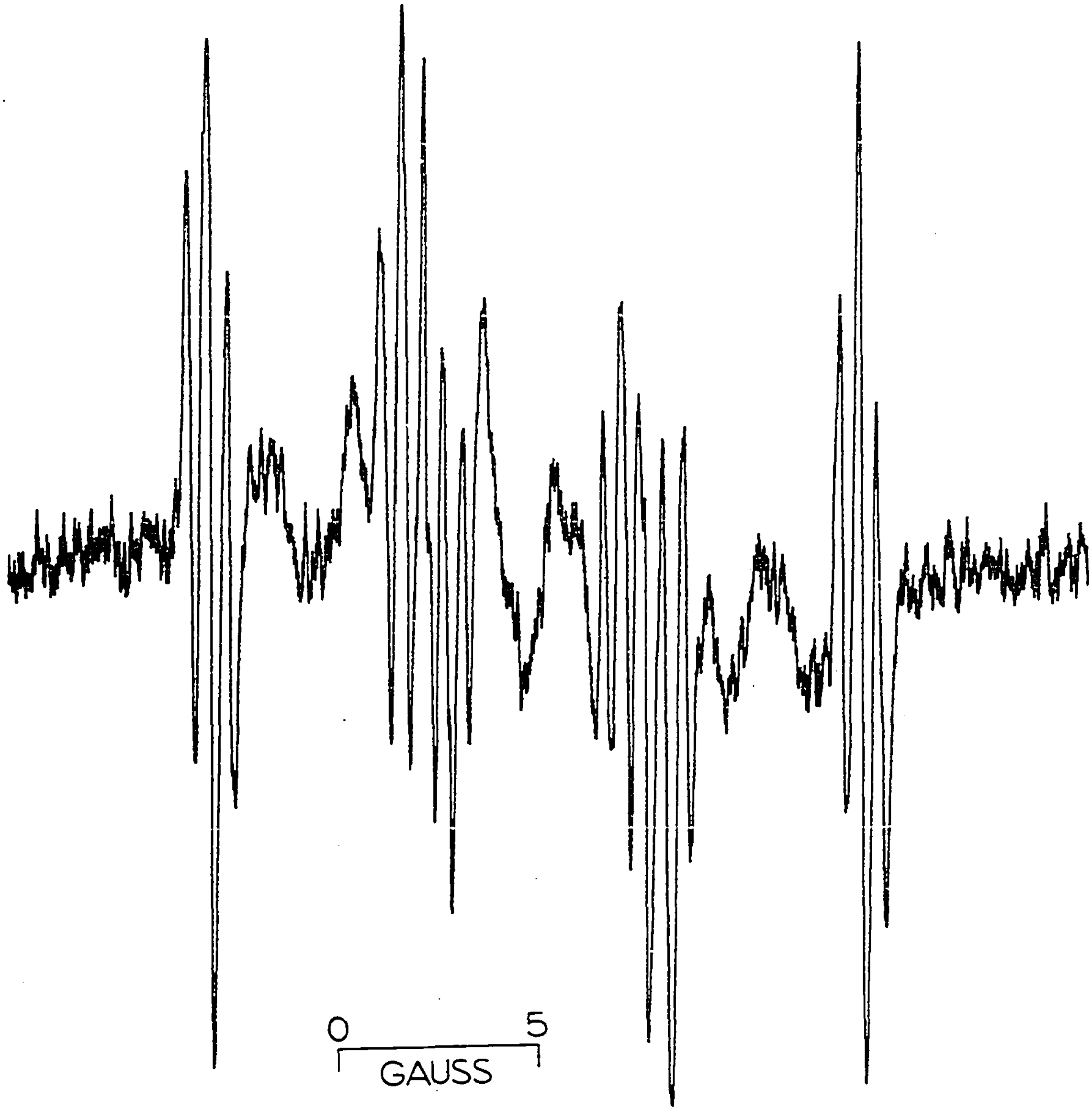


Figure 18. The first derivative esr spectrum obtained by treatment of 2,4-cyclooctadiene-1,6-dione (84) with potassium t-butoxide in DMSO.

When the solutions exhibiting the signal assigned to 96 were exposed to small amounts of air, the signal of 96 disappeared and was replaced by a pentet, $a^H = 1.83$ (4H) G. Further oxidation replaced the pentet with a triplet, $a^H = 2.03$ (2H) G. These signals remain unassigned. On one occasion in which 96 was the only initially observed signal, treatment with oxygen gave a spectrum comprised of two signals, that of *p*-benzosemiquinone, $a^H = 2.39$ (4H) G, and also the esr spectrum of semidione 62.

Electrolysis of diene-dione 84 produced no esr signal. Polarography in deoxygenated acetonitrile (.1 N *t*-butylammonium perchlorate supporting electrolyte) indicated dione 84 to be inert to reduction at potentials below the decomposition potential of the solvent.

When diene-dione 84 was treated with potassium *t*-butoxide under flow conditions, a number of interesting observations were made: (1) at very slow rates (≈0.014 ml/min, detection ≈7 min after mixing) the solution passing through the esr cell window was emerald green and an esr signal was observed (Figure 19) which appeared to arise from two radicals of approximately equal concentrations. One of these signals (that corresponding to the inside triplets in Figure 19) was assigned to semidione 96 seen under static conditions. The other signal was determined to be that of semidione 1; (2) even slower flow rates decreased signal intensity. The signal of

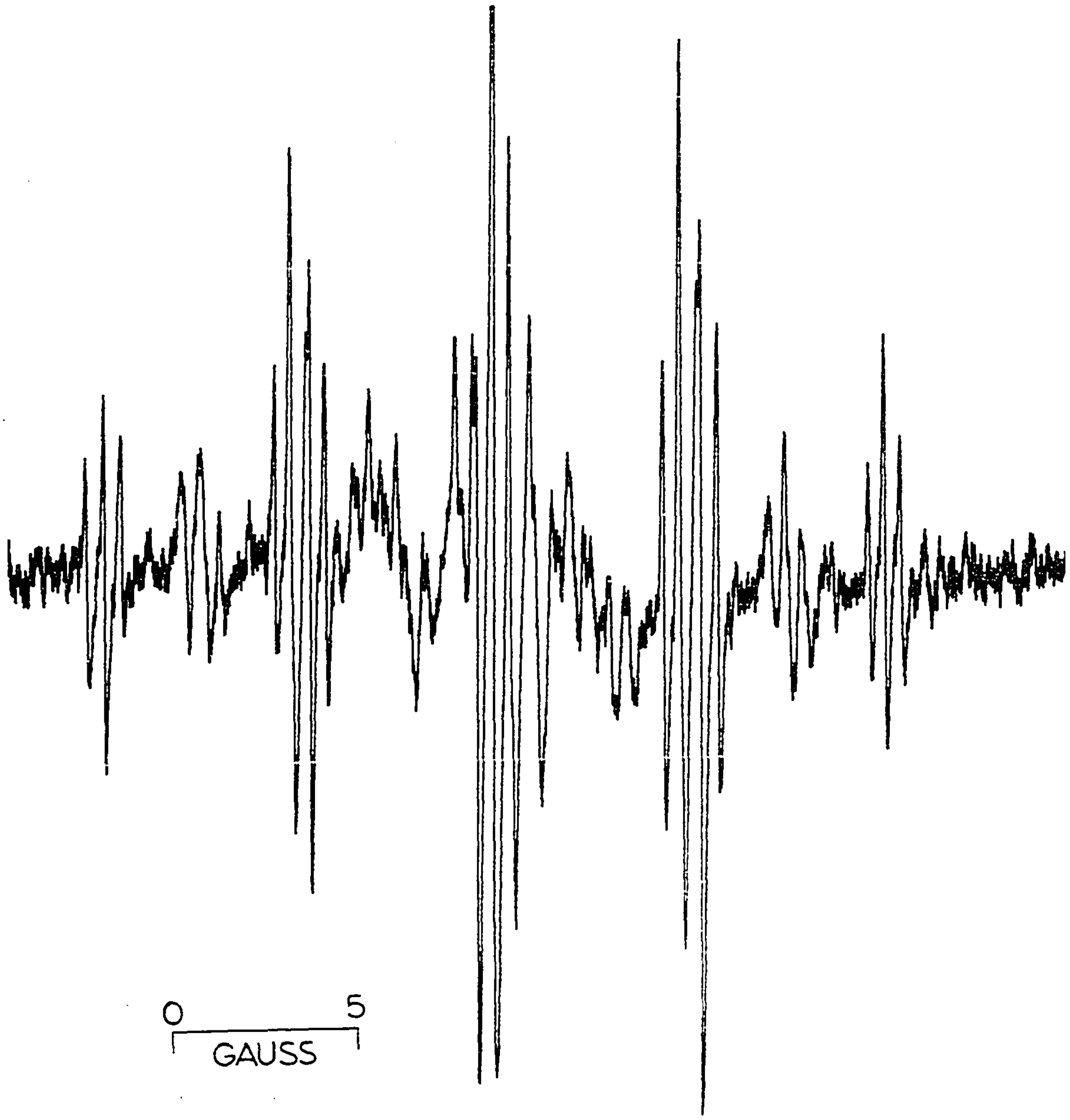


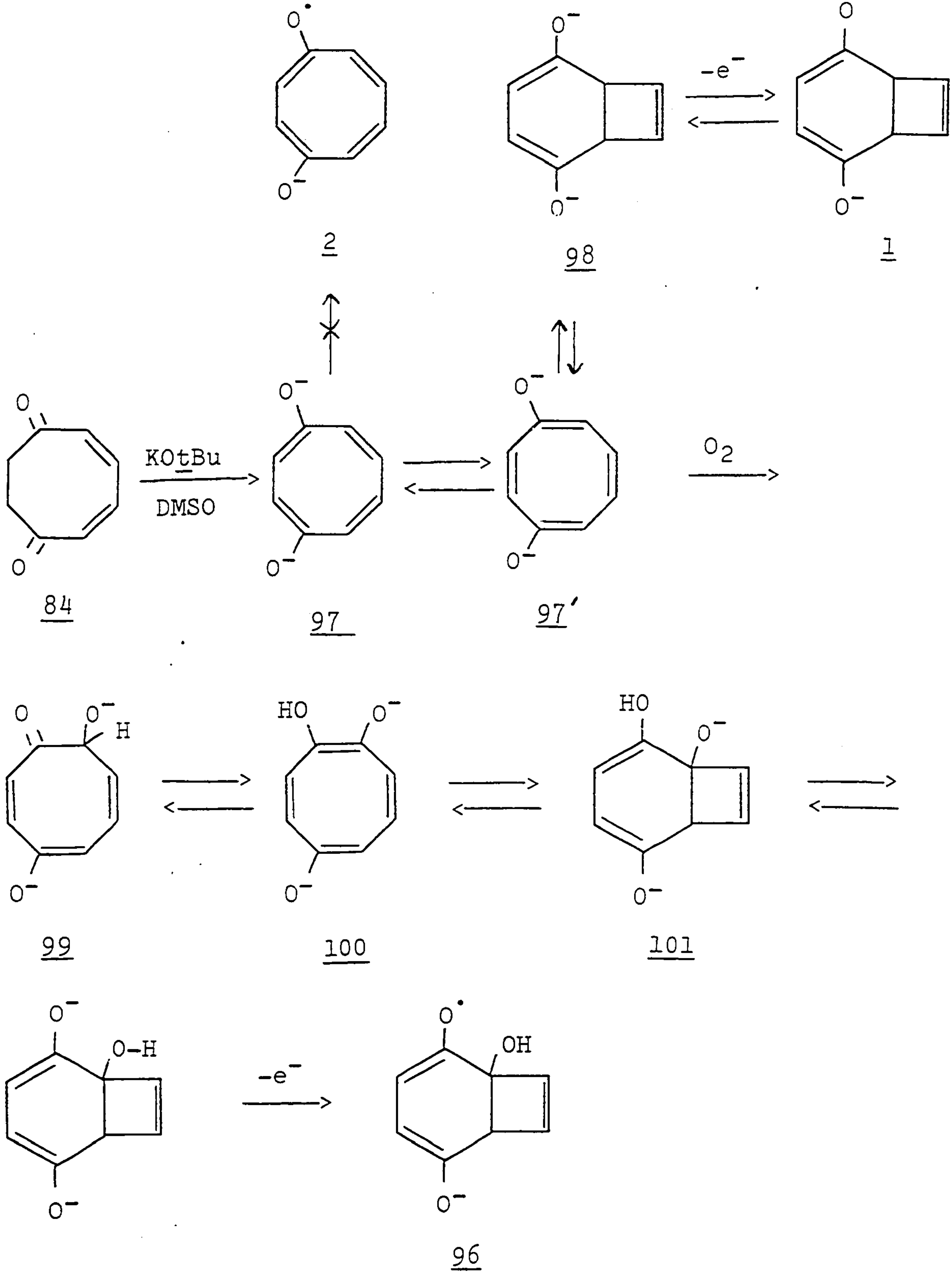
Figure 19. The first derivative esr spectrum obtained from 2,4-cyclooctadiene-1,6-dione in basic DMSO under flow conditions.

semidione 1 appeared to be less intense than that of 96 under these conditions; (3) very fast rates (relatively speaking) resulted in a much weaker signal and the solution in the cell was red; (4) irradiation at 2537Å directly on the esr cell window resulted in the disappearance of the esr signal at flow rates which would otherwise have produced the signal shown in Figure 19; (5) at no time was a signal observed corresponding to the signal assigned to semidione 64 observed earlier upon photolysis of solutions of semidione 1.

Scheme 14 outlines a possible mechanism for the generation of semidiones 96 and 1 from diene-dione 84.

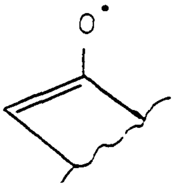
Dianions 97 and 97' are simply bond shift isomers and their interconversion may well be rapid (39, 40, 41). The formation of dianions 97 and 97' is consistent with the color changes noted above. If the bright red solutions are due to diamagnetic dianions 97 and 97', no esr signal would be expected at the faster flow rates. Slower flow rates allow time for 97' to undergo valence isomerization to dianion 98 and oxidation to dianion 99. Either of these dianions, or perhaps one of the other species in Scheme 14 may be responsible for the emerald green color. The disappearance of semidiones 1 and 96 at extremely slow flow (semidione 1, as was noted in an earlier section, is stable for a long time under static conditions) may be due to destruction by any one of a variety of active species in the solution.

Scheme 14



The question arises as to why dianion 97 (or 97') is not oxidized to semidione 2. Enolate anions are reasonably stable entities in basic solution. Therefore, 97 most likely exists in the conventional tub conformation of cyclooctatraene. The coulombic interactions present in a planar, delocalized dianion make its existence improbable (except, perhaps as a transition state for interconversion of 97 and 97' *via* bond shift isomerism). The tub conformation is ideally suited for the valence isomerism of 97' to 98 (also of 100 to 101) *via* a six-center (boat form) Cope rearrangement (86, 87).

On the other hand, one-electron oxidation of 97 would, if the molecule remained in the tub form, produce an enolate anion and a neutral enolate radical. In the tub form it is



difficult to assess the stability of the enolate radical. To form planar semidione 2 a great deal of energy would be required to overcome angle strain, almost certainly more than could be recovered by delocalization of the unpaired electron.

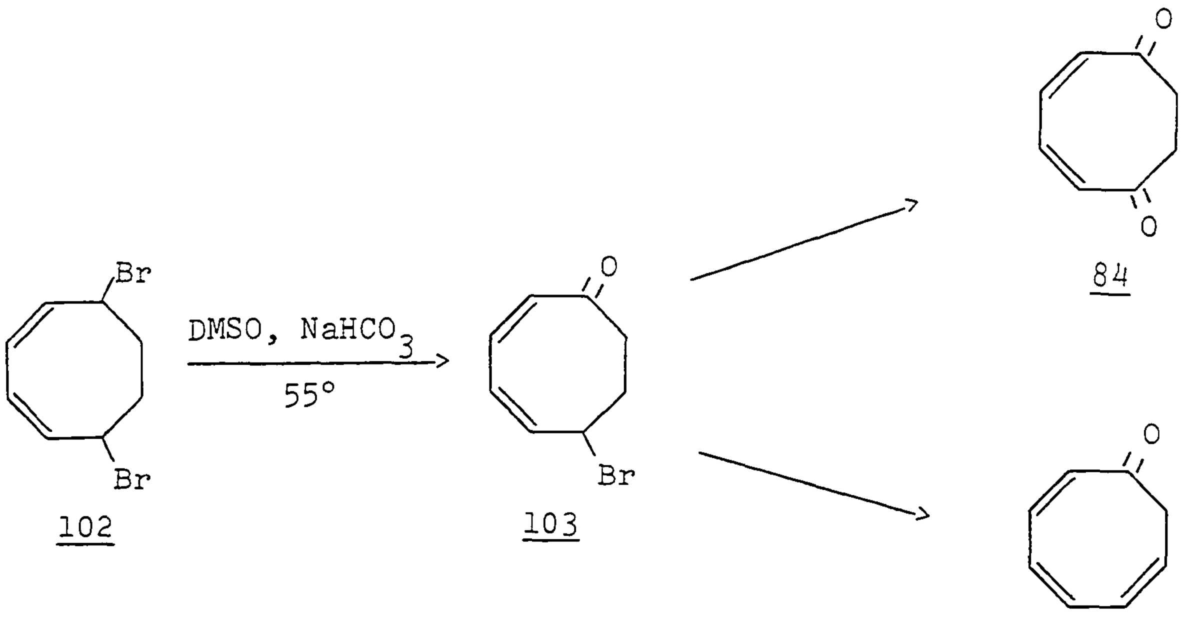
Evidence supporting the relative instability of monocyclic semidione 2 (or the enolate radical) was obtained *via* normal direct current polarographic studies of 2,5,7-cyclooctatriene-1,4-dione (85) in degassed solutions of acetonitrile with t-butylammonium perchlorate (0.1 N) as the supporting electrolyte. A single two-electron reduction with an $E_{1/2}$ of -1.00 V (vs SCE) was obtained. The facile two-electron reduction may indicate, in analogy to the reduction of cyclooctatetraene (88), that the second electron is more easily introduced than the first, and also, that the two-electron reduction product is thermodynamically more stable than the one-electron reduction product. This indicates that dianion 97 may, in fact, be greatly favored over semidione 2. The $E_{1/2}$ of -1.00 V (vs SCE) for the two-electron reduction of 85 is much lower than that of the two-electron reduction of cyclooctatetraene ($E_{1/2}$ = -1.5 (vs SCE)). The higher value for the cyclooctatetraene anions may mean that they require additional energy to achieve planarity while 2 and 97, which remain in the tub form, do not.

It is possible that semidione 1 is not formed by the process shown in Scheme 13 but, rather, is formed from dione 49 present as a contaminant in diene-dione 84. The pmr spectrum of 84 was void of any resonances characteristic of 49 although this is a poor criterion of purity, since the esr technique is capable of detecting concentrations on the order of 10^{-6} M. However, it was observed that a single batch of diene-dione 84 while giving the signal of 1 under flow conditions did not give that signal under static conditions. While not ruling out the possibility of contamination by 49, this result does argue against it. Even if this were the case, Scheme 13 could still be valid for the generation of semidione 96.

To confirm or negate the argument above, an alternate synthesis (one not involving bicyclic dione 49 as an intermediate) of 2,4-cyclooctadiene-1,6-dione (84) is required. The following section will describe work directed toward alternate syntheses of diones 84 and 85 or other acceptable precursors of the monocyclic semidione 2.

Unsuccessful Attempts to Synthesize Precursors of 5,7-Cyclooctadiene-1,4-semidione

DMSO oxidation of 1,6-dibromo-2,4-cyclooctadiene (102) gave good yields of 6-bromo-2,4-cyclooctadiene-1-one (103). More forceful conditions did not produce 84, rather, elimination to form cyclooctatrieneone (104) was evident. It was



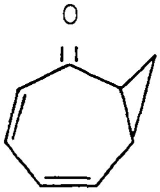
102

103

84

104

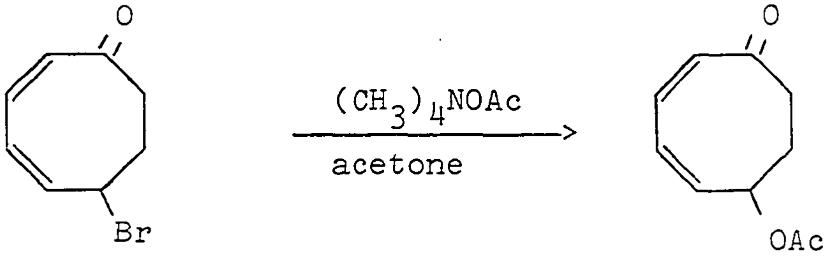
later reported (89) that the reaction of dibromide 102 with strong bases in DMSO gives trienone 104 and homotropone (105).



105

It appears that elimination of the second bromide ion is favored over oxidation.

Bromo ketone 103 has been reported to give no signal in basic DMSO (22). The acetoxy ketone 106 gave a weak signal,

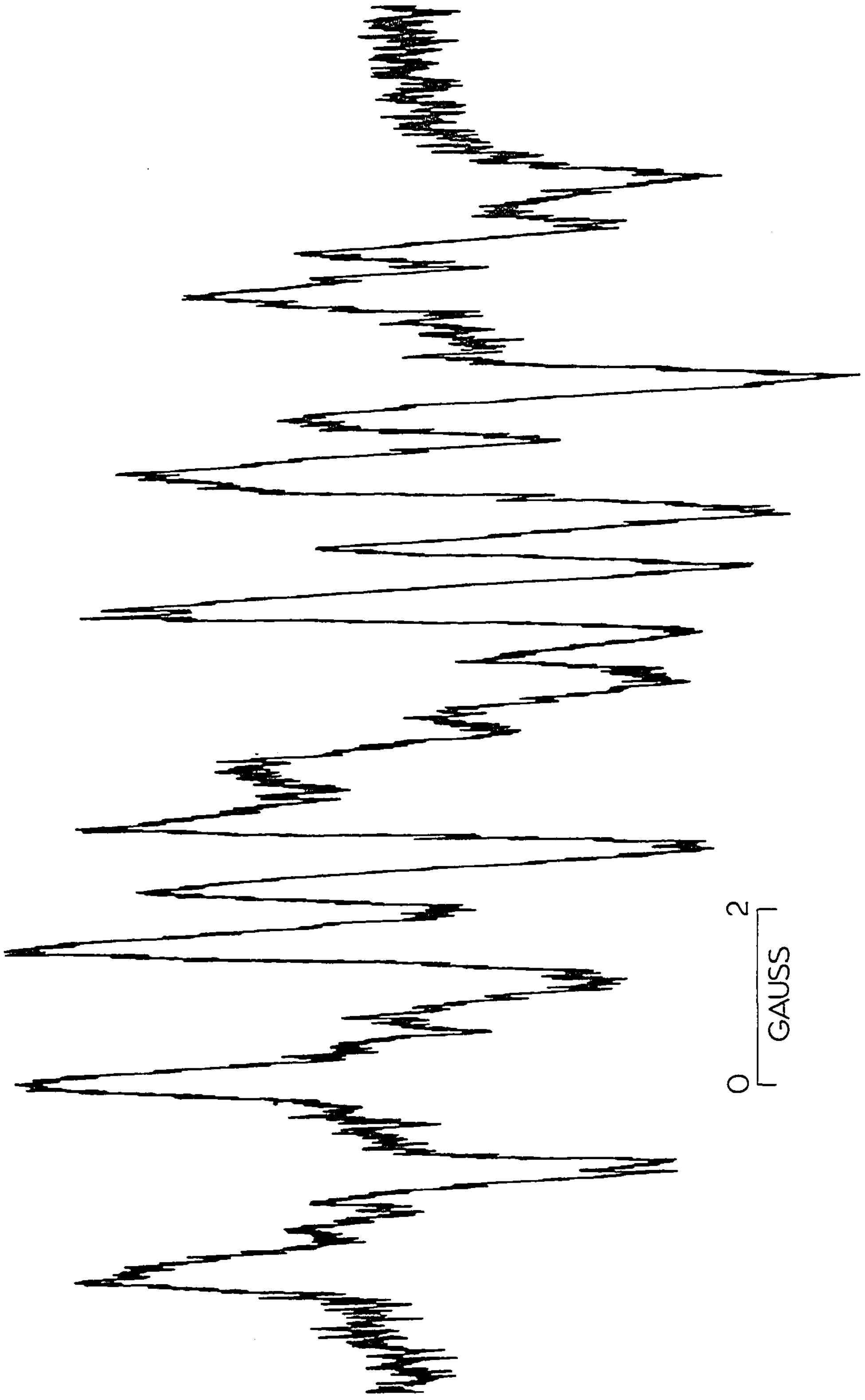


103 106

a^H = 5.3 (1H), 3.6 (1H), 2.2 (1H), and 0.6 (1H) G, in basic DMSO which got stronger upon addition of traces of oxygen (Figure 20). No structure has been assigned to this radical. Larger amounts of oxygen replaced this signal with that of p-benzosemiquinone (a^H = 2.40 (4H) G).

It has been shown that when treated with oxygen in the presence of a radical initiator cyclic dienes form polymeric

Figure 20. The first derivative esr spectrum obtained upon treatment of acetoxy ketone 106 with basic DMSO and traces of oxygen.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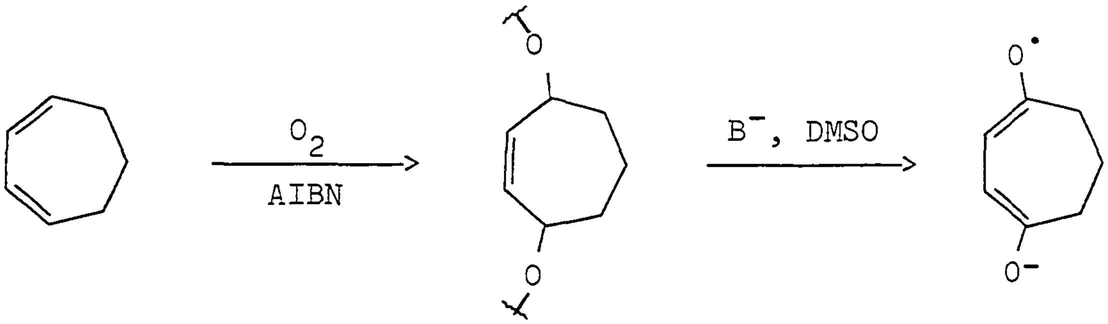
2

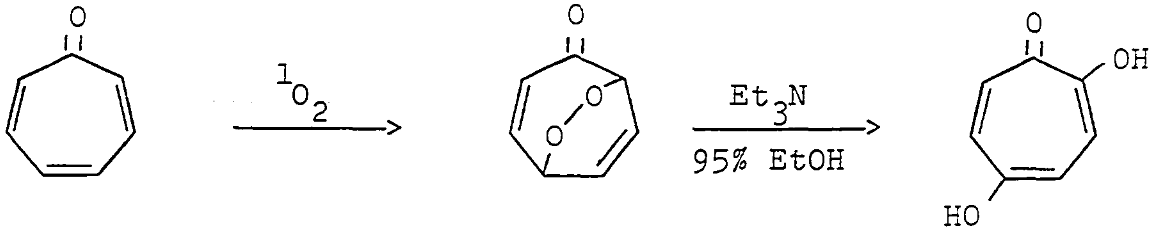
peroxides which, upon treatment with potassium t-butoxide in



DMSO, give the corresponding semidione.[4] However, reaction of cyclooctatetraene with oxygen, with azobisisobutyronitrile (AIBN) as a radical initiator, resulted in the formation of red tarry residues which gave only weak, broad esr signals when treated with basic DMSO.

Oda and Kitahara have reported that addition of singlet oxygen to tropone gives an unstable endoperoxide which can be converted to the corresponding dihydroxy compound upon basic hydrolysis (90) (Scheme 15). Accordingly, sensitized

Scheme 15



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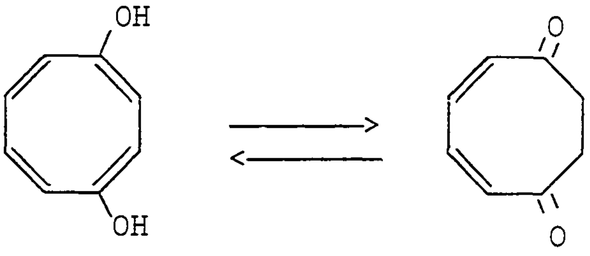
[4] Dr. Y. Kosugi, private communication, Iowa State University, Ames, Iowa, 1974.

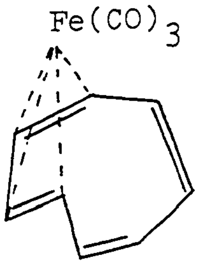
irradiation of cyclooctatetraene in oxygen-saturated solutions followed by basic hydrolysis gave a dark brown oil. The nmr of this material showed predominantly aromatic resonances (δ 7.1-7.3) not at all in accord with diol 107 or ketone 84.



107 84

Treatment of this crude product with potassium *t*-butoxide in incompletely deoxygenated DMSO gave a weak signal which was solved for two hydrogens with splitting of 2.86 gauss and one hydrogen of 0.88 gauss. This signal has not been assigned.

Cyclooctatetraeneirontricarbonyl 108 has been shown to have a planar diene unit (91). It was speculated that this arrangement should make the Diels-Alder addition of singlet oxygen more favorable than to the tub-like cyclooctatetraene.

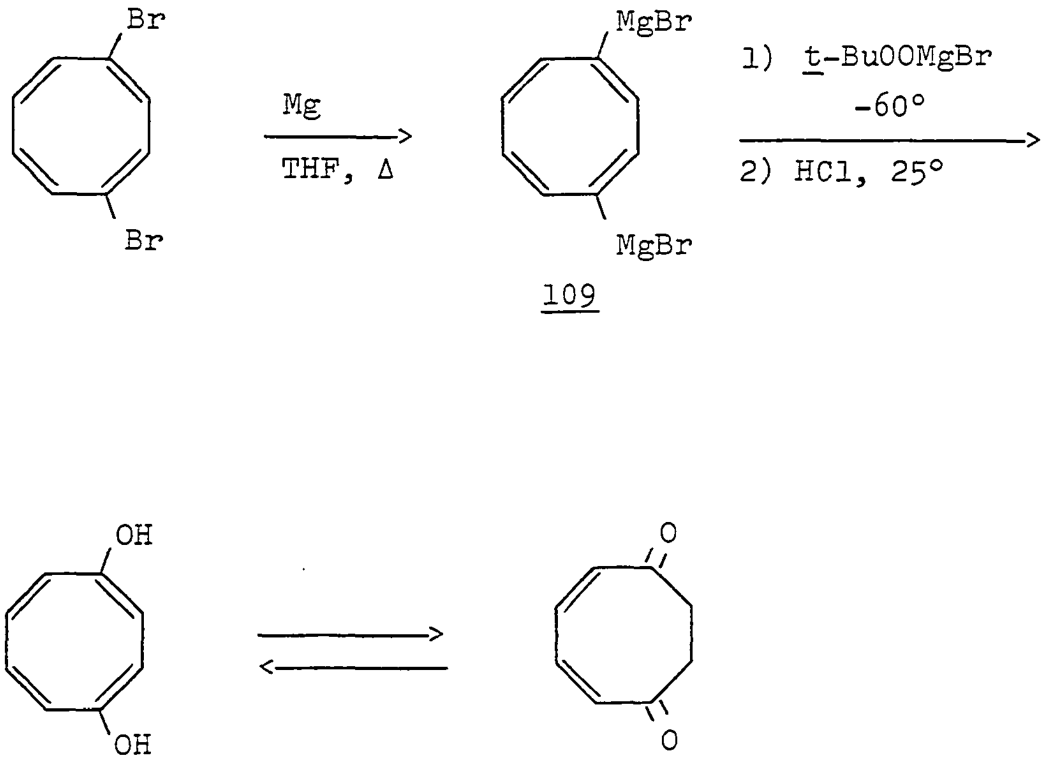


108

However, extended irradiation of oxygenated solutions of 108 with sensitizer resulted in near quantitative recovery of 108 along with a trace of brown, insoluble residue - presumably iron oxide.

Lawesson and Yang reported that the reaction of aryl Grignard reagents with the magnesium salt of *t*-butyl hydroperoxide gives excellent yields of phenols (92). This report led us to propose the reaction sequence shown in Scheme 16 for the synthesis of 84. The alkali metal dianions of

Scheme 16



109

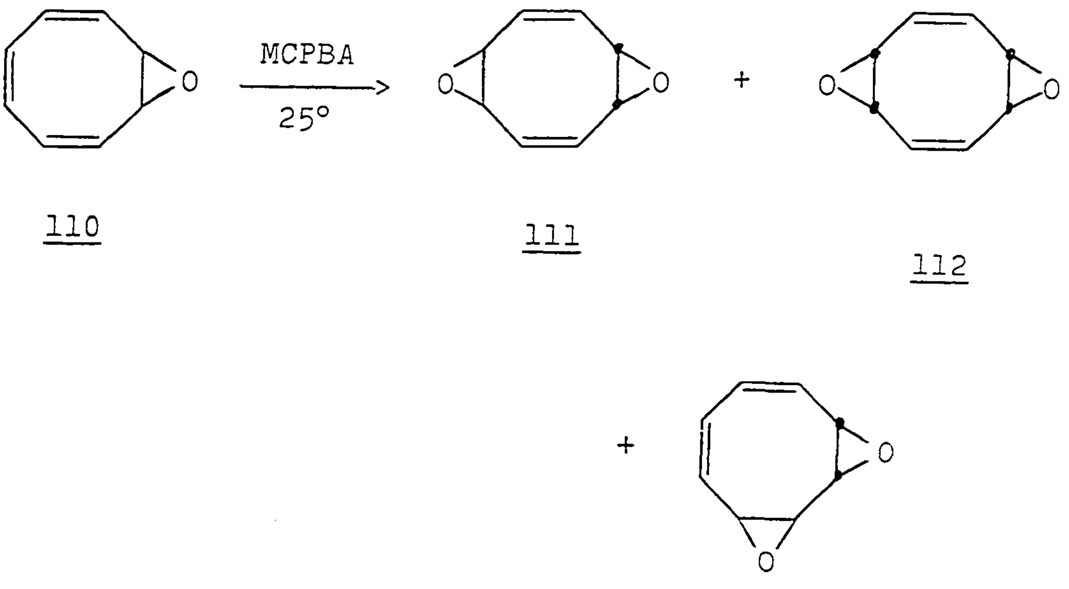
107

84

cyclooctatetraene are well characterized (23). However, there has been no report of the generation of the di-Grignard reagent **109**. Generation of **109** by the same method reported for the generation of cyclooctatetraenemagnesium bromide (93) and treatment with *t*-butylperoxydimagnesium bromide followed by acid hydrolysis gave a product which, after chromatography on silica gel, displayed a carbonyl absorbance in the infrared spectrum. However, the proton magnetic resonance spectrum showed predominantly aromatic resonances and no resonances characteristic of **84** (83).

Anastassiou and Reichmanis have reported (94) the synthesis of diepoxides **111**, **112** and **113** from cyclooctatetraene epoxide (**110**) and *m*-chloroperbenzoic acid (Scheme 17).

Scheme 17

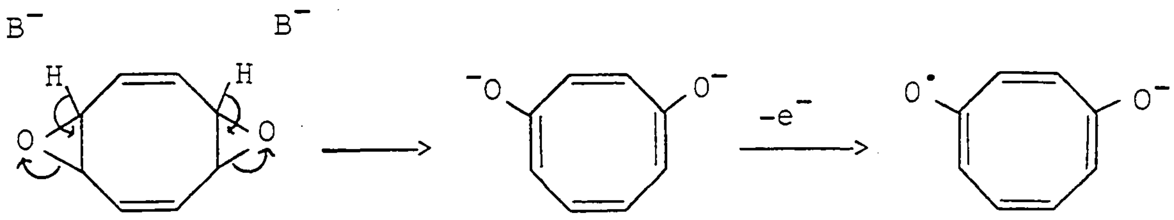


110 **111** **112**

113

We thought that diepoxides 111 and 112 might product semidione 2 in basic DMSO (Scheme 18).

Scheme 18

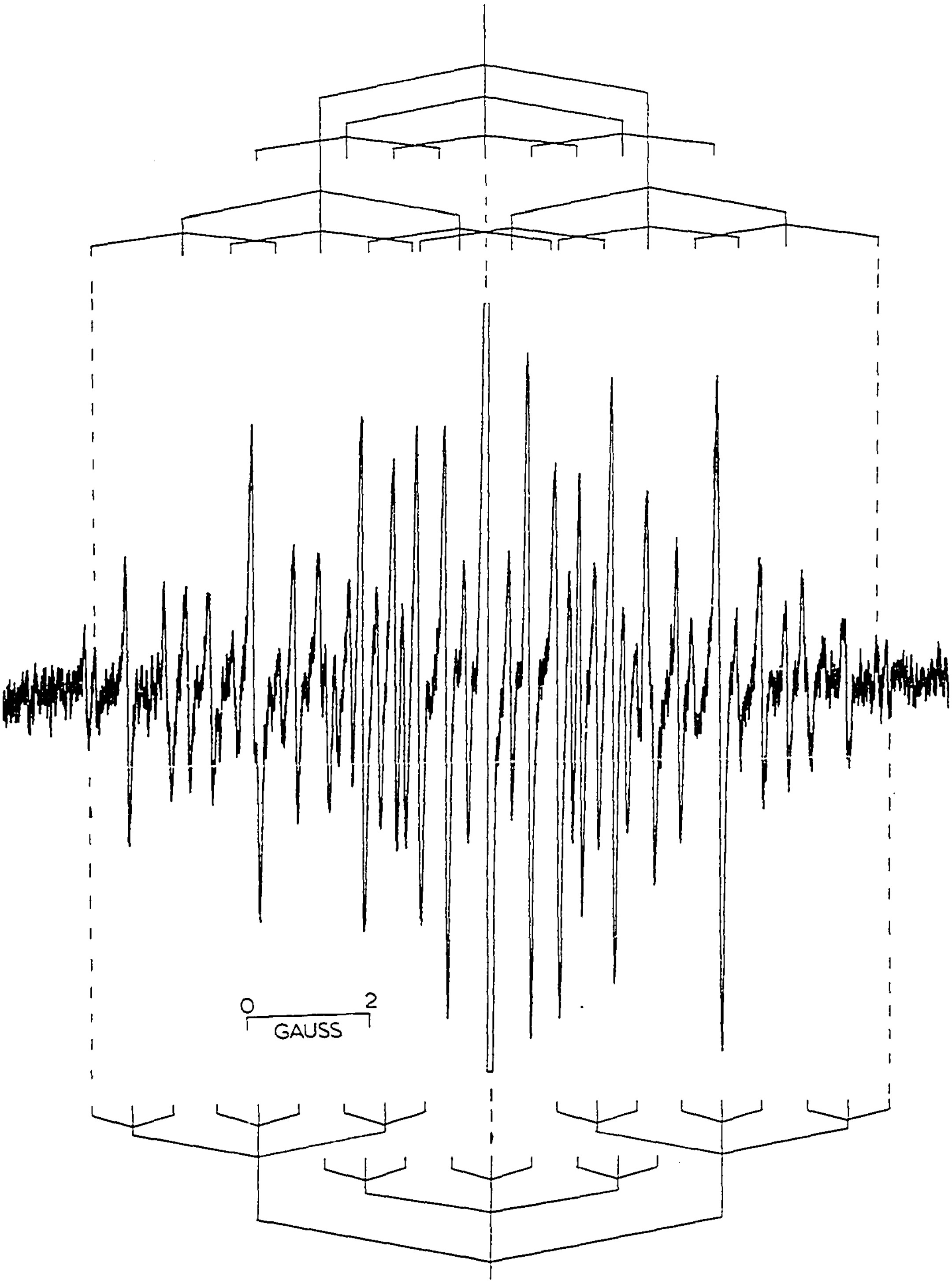


111 97' 2

The epoxidation of 110 was performed as reported in the literature (94). Purification by the reported technique (column chromatography on neutral alumina at -15°) gave poor separation of the products. Only diepoxide 112 was obtained in a pure state.

Treatment of pure 112 with a nitrogen deoxygenated solution of potassium t-butoxide in DMSO gave no esr signal. Addition of oxygen had no effect. When a somewhat impure sample of 112 (contaminated primarily with 111 and 113 as determined by pmr) was treated with basic DMSO under slow flow conditions, an esr signal was observed (Figure 21). The spectrum does not solve as a single signal. A possible

Figure 21. The first derivative esr spectrum obtained by treating crude diepoxide 112 with base and DMSO under flow conditions.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2
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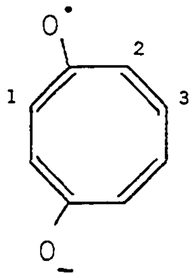
solution for two radicals is shown in Figure 21. The top diagram indicates a signal consisting of three triplets of a^H = 1.50 (2H), 2.26 (2H), and 2.67 (2H) G.

The bottom solution also shows three pairs of hydrogens, a^H = 0.66 (2H), 2.08 (2H), and 3.81 (2H) G. Either of these solutions is consistent with spin density calculations (both Hückel and McLachlan) on planar 5,7-cyclooctadiene-1,4-semidione (2) which indicate $a_1^H < a_2^H, a_3^H$.[5] While the possibility exists that semidione 2 was indeed generated, the impurity of the substrate and somewhat questionable solution of the spectrum in Figure 21 make such a conclusion speculative. The hfsc's are inconsistent for assignment of one of the radicals as 1,2-semidione 18 (cited in the Historical).



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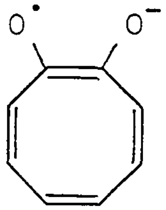

18

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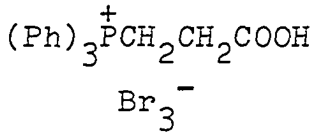
[5] C.S.C. Chung, private communication, Iowa State University, Ames, Iowa, 1972.

Another approach (Scheme 19) to 2,5,7-cyclooctatriene-1,4-dione (85) was envisioned following Kitahara and coworkers' report (95) of the synthesis of 2-cyclooctene-1,4-dione (116). Treatment of diketone 116 with a stoichiometric amount of cupric bromide in a refluxing mixture of ethyl acetate and chloroform (96) gave, after workup, a crude product whose pmr spectrum was not at all in keeping with the expected dibromide 117. The pmr spectrum showed significant aromatic absorbances and broad alkyl resonances (δ 1.5-2.8) approximately two times as large as expected. Nevertheless, this crude product was treated with lithium carbonate and lithium chloride in dimethylformamide at 75° to give a crude product exhibiting little olefinic and disproportionately large alkyl resonances in the pmr spectrum.

Attempted bromination of 116 with N-bromosuccinimide using chemical and/or photolytic initiation resulted in recovery of starting material. 2-Carboxyethyltriphenylphosponium perbromide has been shown to be an effective alpha-brominating reagent for ketones, unaffected by α,β-

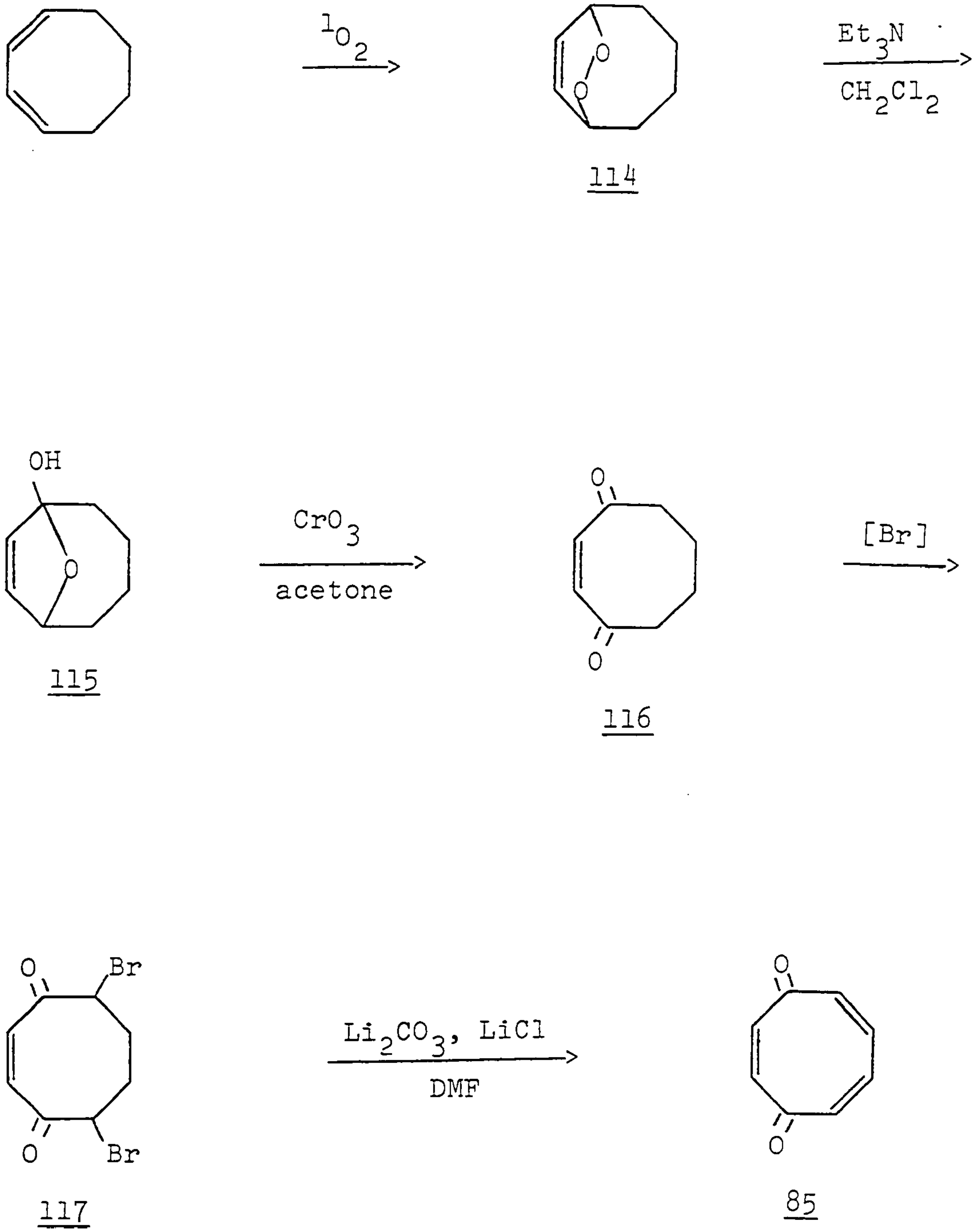


$$(\mathrm{Ph})_3\overset{+}{\mathrm{P}}\mathrm{CH_2CH_2COOH} \quad \mathrm{Br_3}^-$$

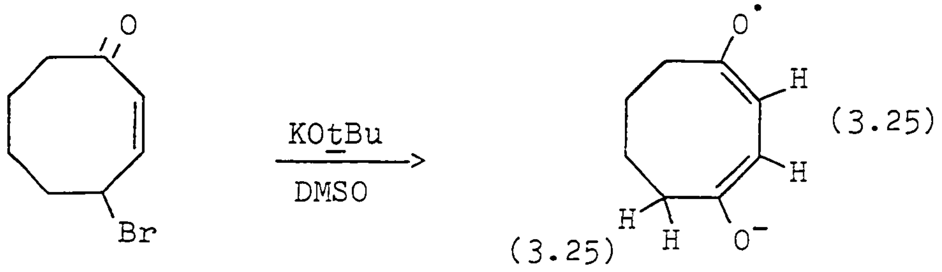
unsaturation (97). However, treatment of 116 with this reagent resulted in complete bromination of the double bond.

With diketone 116 in hand it was of interest to generate its semidione since Goettert has reported that

Scheme 19


$^1O_2$
114
Et_3N
CH_2Cl_2
OH
115
CrO_3
acetone
116
[Br]
Br
Br
117
Li_2CO_3, LiCl
DMF
85

treatment of 4-bromocyclooct-2-ene-1-one (118) with base and DMSO gives an esr signal consisting of six equivalent hydrogens of 3.25 gauss which was assigned to cyclooctane-1,4-semidione (119).

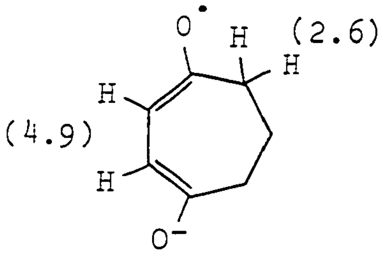


118

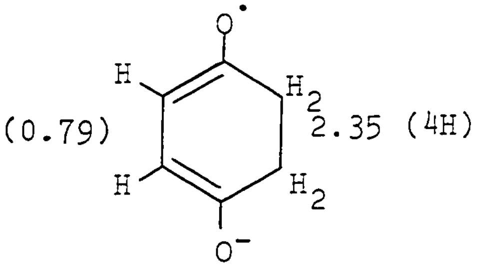
119

It was surprising, to say the least, to find that treatment of analytically pure 118 with potassium t-butoxide in freeze-pump-thaw degassed DMSO gave not the simple seven line spectrum observed by Goettert but, rather, a very complex spectrum with a lot of hyperfine structure (Figure 22).

At this point, Goettert's results were reexamined. The value of 3.25 gauss for the hydrogens on the spin label is much too low when compared to cycloheptane-1,4-semidione (66) (74, 98) and cyclohexane-1,4-semidione (120) (98). In

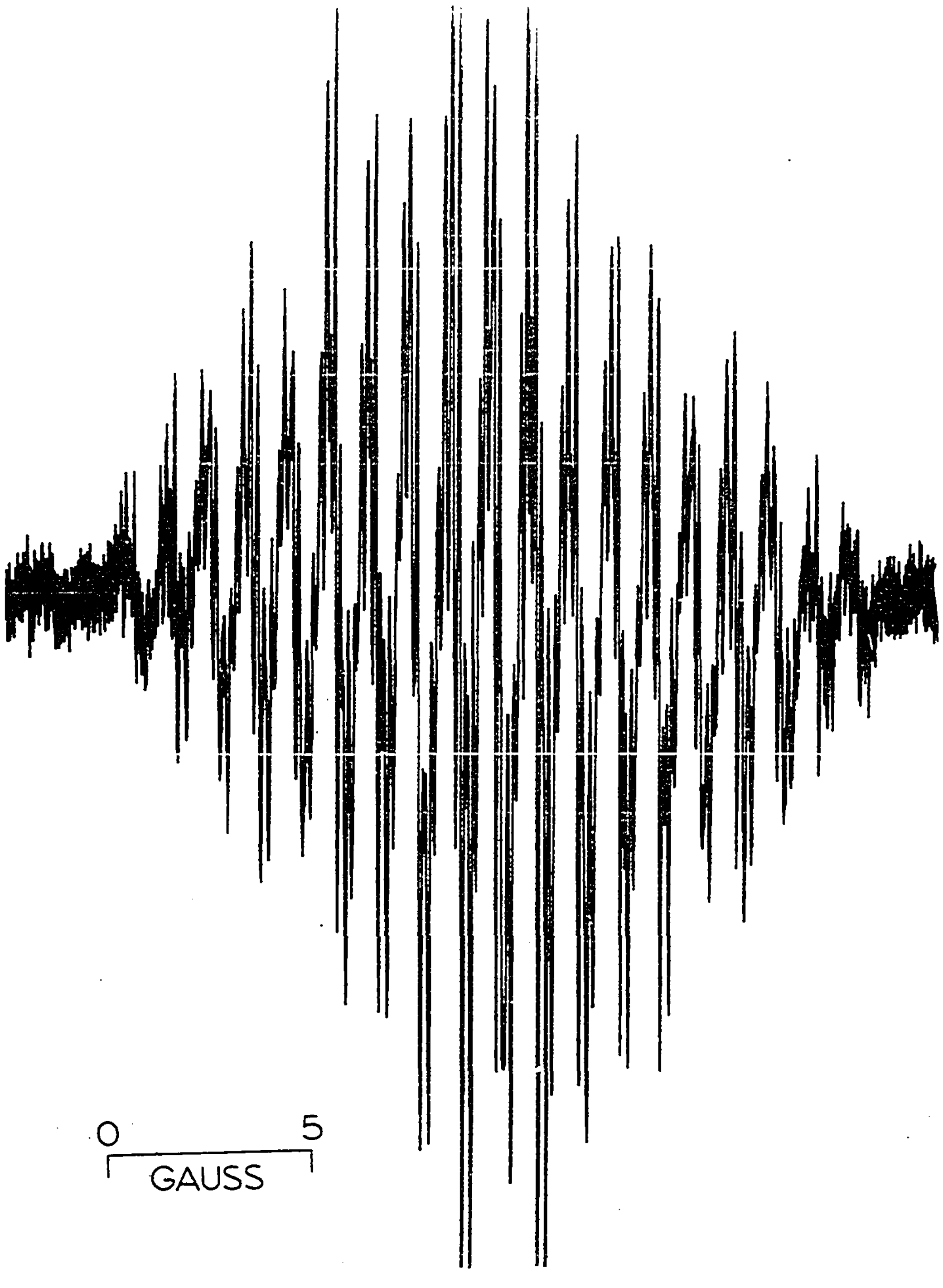


66



120

Figure 22. The first derivative esr spectrum obtained upon treatment of 2-cyclooctene-1,4-dione (116) with basic DMSO.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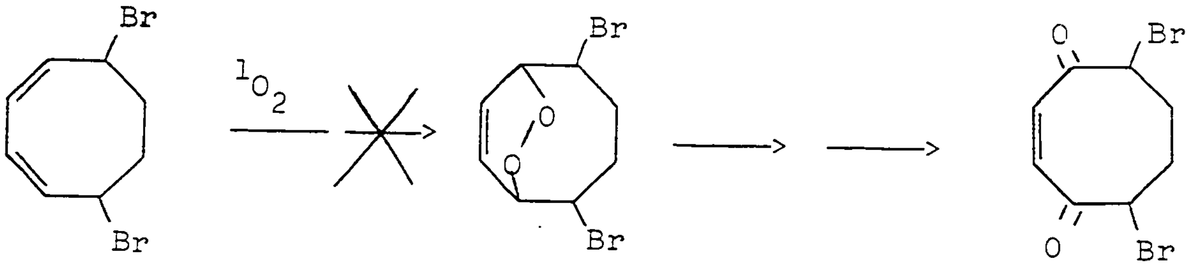
addition, examination of Prentice-Hall molecular models indicates that the alpha hydrogens of cyclooctane-1,4-semidione (119) have approximately the same dihedral angle with the p orbital of the spin label as do those of cycloheptane-1,4-semidione (66). Thus, conformational equilibria neglected, the value of 3.25 gauss for the alpha hydrogens is too high.

Solution of the spectrum shown in Figure 22 as three pairs of equivalent hydrogens (2H on spin label, 2 α-H equatorial, 2 α-H axial) or as a triplet of pentets (2H on spin label, 4 α-H equivalent) were unsatisfactory. Both solutions conflicted with the observed intensities and/or number of lines. A strong possibility exists that the observed spectrum is a mixture of radicals.

The addition of singlet oxygen to 1,6-dibromo-2,4-cyclooctadiene (102) appeared to offer an alternate method for introduction of the alpha bromine atoms (Scheme 20); however, 102 showed no tendency to add singlet oxygen even upon extended irradiation.

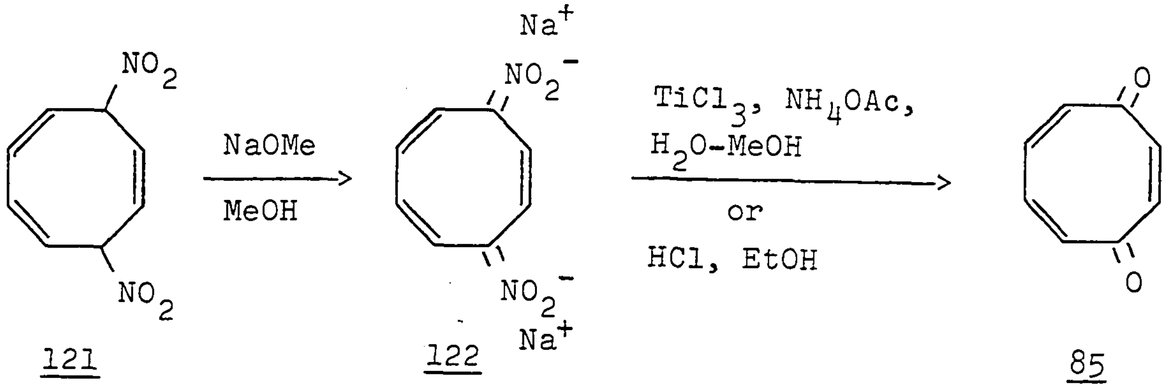
Scheme 20



102

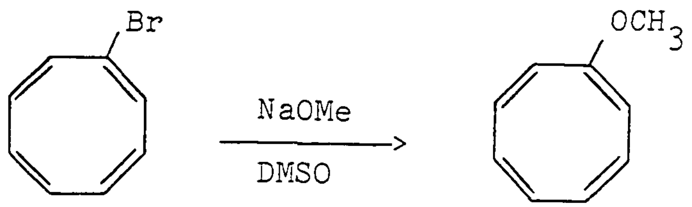
A report (99) describing the synthesis of disodium-2,5,7-cyclooctatriene-1,4-dinitronate (122) led us to attempt the transformations outlined in Scheme 21.

Scheme 21



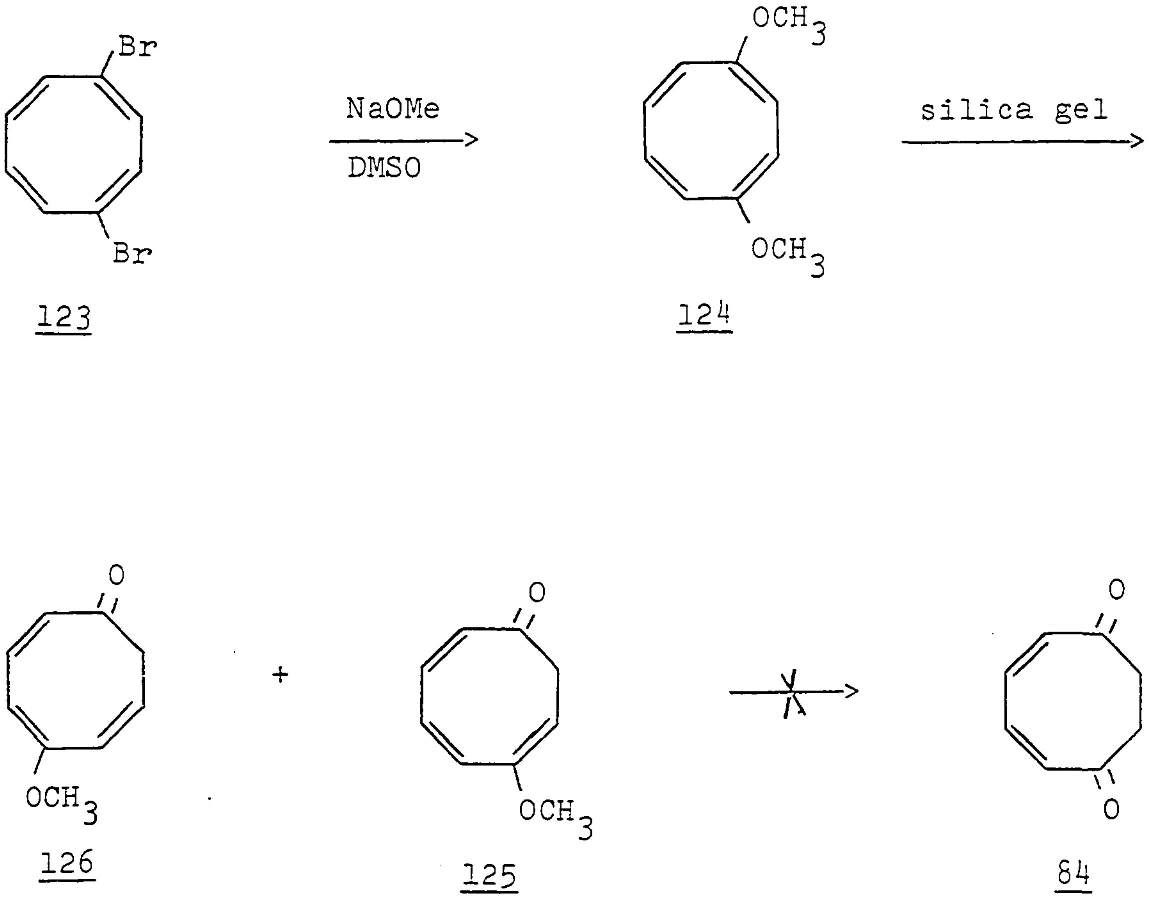
Treatment of methanol solutions of the dinitronate salt 122 with aqueous, buffered (NH_4OAc, pH ~6) titanium trichloride (100) or, alternatively with concentrated hydrochloric acid (the Nef reaction (101)) gave complex crude product mixtures. The spectral data obtained from these mixtures were not consistent with the presence of 85. Neither crude product gave an esr signal when treated with potassium t-butoxide in DMSO.

In analogy to the reported (102, 103) reaction of bromocyclooctatetraene with sodium methoxide in DMSO, 1,4-dibromocyclooctatraene (123) was treated with sodium methoxide in DMSO to give good yields of a crude product whose spectral



data was consistent with 1,4-dimethoxycyclooctatetraene (124) (Scheme 22). Elution from a column of silica gel gave 124

Scheme 22



along with a considerable quantity of a compound whose spectral data were consistent with a mixture of the vinyl ether 125 and its isomer 126. Since 1,4-dibromocyclooctatetraene has been shown to be contaminated with significant amounts of 1,5-dibromocyclooctatetraene (104), the presence of 126 can be rationalized.

Surprisingly, 125 and 126 appeared to be quite resistant to further hydrolysis. Although the reaction sequence shown in Scheme 22 appeared to be the most promising alternate route to dione 84 the hydrolysis of 125 and 126 was not studied in depth.

EXPERIMENTAL

Reagents

Dimethyl sulfoxide (DMSO) was distilled from CaH_2 at 15-25 Torr and stored over 4A molecular sieves. Potassium t-butoxide was obtained commercially (MSA Research Corporation), stored in a desiccator over $CaCl_2$, and used without further purification. Unless otherwise noted, solvents were reagent grade and were used as received.

Preparation of Semidiones

Fused silica flat cells with inverted U-type mixing chambers were used for the generation of radical anions under static conditions by methods previously described (105). The cell shown in Figure 23 was used for generation of radical anions using potassium t-butoxide and DMSO when pump-freeze-thaw degassing was required.

Electrolytic reductions were carried out in fused silica flat cells with a platinum anode and a mercury pool extending into the cell window as the cathode. Electrolytic solvents (distilled from CaH_2 and stored over 4A molecular sieves) were .1 N in t-butylammonium perchlorate which was stored in a desiccator over $CaCl_2$. Deoxygenation of electrolytic solutions was accomplished by nitrogen bubbling.

Electrolytic reductions requiring freeze-pump-thaw degassing were accomplished in a cell previously described by

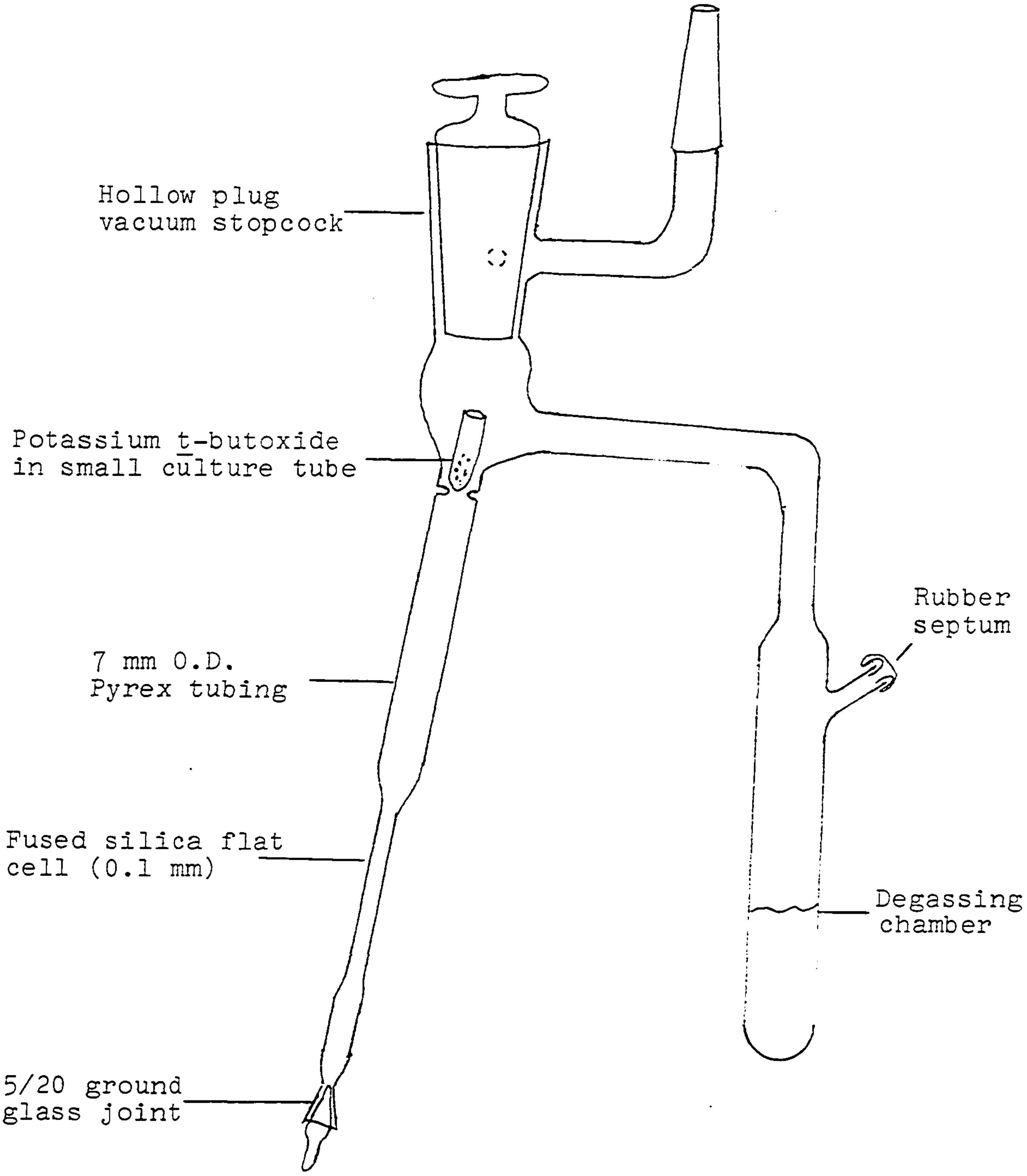


Figure 23. Esr cell used for KO*t*Bu/DMSO experiments requiring freeze-pump-thaw degassing.

Russell and coworkers (106). A Heathkit L. V. Power Supply Model IP-27 was used as the current source.

Flow experiments were performed as described by Schmitt (13). Irradiations of solutions in the esr cavity were performed with a Pen-Ray Lamp (Ultraviolet Products) rated at 14 watts with major (90%) emission at 2537Å.

Recording and Simulation of ESR Spectra

The esr spectra were recorded using either a Varian V-4502 spectrometer with 100 KHz field modulation and a 9-inch magnet, equipped with a Fielddial magnetic field regulator, or a Varian E-3 spectrometer with a 4-inch magnet and 100 KHz field modulation. The esr spectra were simulated on a JNM-RA-1 spectrum accumulator (Japan Electron Optics Company). The program used fit a variable Lorentzian line width to a stick diagram of the spectrum.

Characterization of Compounds

Pmr spectra were recorded on either a Varian A-60 spectrometer or a Perkin Elmer/Hitachi R-20B NMR spectrometer. Chemical shifts (δ) were measured in parts per million relative to TMS taken as 0.00. Ir spectra were recorded on a Beckman Model IR-12, a Beckman Model IR-18A, or a Beckman Model IR-4250 Infrared Spectrometer in chloroform solution unless noted otherwise. Low resolution mass spectra were obtained on an Atlas CH4 spectrometer. High resolution mass spectra were obtained on an AEI-902 spectrometer. Preparative gas chromatography was performed on an Aerograph A-90-P chromatograph. Melting points were obtained on a Thomas Hoover Capillary Melting Point Apparatus and were uncorrected. Carbon and hydrogen microanalysis were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Preparation of Compounds

Column chromatography was performed using slurry packed 60-200 mesh silica gel (Baker) or Woelm neutral aluminum oxide of the activity grade indicated. Drying of organic phases was accomplished with anhydrous magnesium sulfate unless otherwise noted. *In vacuo* solvent removal was accomplished on a rotary evaporator at aspirator pressures.

General procedure for the addition of photochemically generated singlet oxygen to dienes

Irradiations were performed through a water-cooled Pyrex immersion well in a cylindrical vessel of ≈ 1.2 ℓ volume using a Sylvania DVY 650 W tungsten-halogen projector lamp operated at 45 volts. Oxygen uptake was measured by a 500 ml addition funnel connected to a leveling bulb filled with mineral oil. A water-cooled condenser was placed on the inlet port of the reaction vessel to minimize solvent evaporation. The solution was vigorously stirred by a magnetic stirring bar.

7,8-Dimethyl-3,4-benzobicyclo[4.2.0]octa-3,7-diene-2,5-dione (42d)

Sublimed naphthoquinone (3.16 g, 0.02 mol) and 2-butyne (4.3 g, .08 mol) were dissolved in 250 ml of nitrogen deoxygenated benzene in a Vycor flask equipped with a cooling coil, magnetic stirrer and septum. The solution was irradiated with a 275 W sunlamp for 44 hr after which time pmr analysis of an aliquot revealed complete reaction of the quinone. Removal of the solvent in vacuo left 5.64 g of a dark red oil which was eluted from a silica gel column (CCl_4-ethyl acetate; 95:5) to give the desired material as the third major fraction. Sublimation at 57° (0.04 Torr) 0.213 g (5.0%) of 42d as a powdery tan solid: mp 116-117°; pmr ($CDCl_3$) δ 1.67 (d, 6H, $J = 1.5$ Hz), 3.80 (br s, 2H), and 7.58-8.16 (sym m, 4H) [Lit. (107) mp 120-121°; pmr ($CDCl_3$) δ 1.68 (s, 6H), and 3.81 (s, 2H)].

1,6,7,8-Tetramethyl-3,4-benzobicyclo[4.2.0]octa-3,7-diene-2,5-dione (42e)

A solution of 1.86 g (0.01 mol) of sublimed 2,3-dimethylnaphthoquinone and 2.16 g (0.04 mol) of 2-butyne was irradiated as described above for 42d. After 70.5 hr, the solvent was removed to afford a red oil. Unreacted 2,3-dimethylnaphthoquinone was removed by shaking an ethereal solution of the residue with a 10% solution of sodium dithionite in 1 N aqueous NaOH. The ether layer was dried and removal of solvent gave a yellow crystalline solid. The solid was recrystallized first from pentane-CCl_4 and then CCl_4 to afford 0.132 g (5.5%) of 42e as white plates: mp 135-136.5°; pmr ($CDCl_3$) δ 1.47 (s, 6H), 1.51 (s, 6H), and 7.61-8.19 (sym m, 4H) [Lit. (107) mp 139-140°; pmr ($CDCl_3$) δ 1.48 (s, 6H), and 1.51 (s, 6H)].

1,6-Dimethyl-8-phenyl-3,4-benzobicyclo[4.2.0]octa-3,7-diene-2,5-dione (42f)

A solution of 2.45 g (0.013 mol) of 2,3-dimethylnaphthoquinone and 1.90 g (0.019 mol) of phenylacetylene in 250 ml of benzene was irradiated as described above for 42d. The reaction was essentially complete after 10 hr. The benzene was removed *in vacuo* and traces of unreacted quinone were removed by shaking an ethereal solution of the resulting yellow solid with 100 ml of 1 N NaOH containing 10 g of sodium dithionite. The ethereal solution was dried and the solvent removed to give an oily, off-white solid. Two recrystallizations from ethanol-Skelly B (4:1) afforded 1.36 g (36%) of 42f as white plates: mp 140.0-140.7°; pmr ($CDCl_3$) δ 1.63 (s, 3H), 1.78 (s, 3H), 6.58 (s, 1H), 7.23-7.59 (m, 5H), and 7.65-8.30 (sym m, 4H) [Lit. (107) mp 140-141°; pmr ($CDCl_3$) δ 1.64 (s, 3H), 1.78 (s, 3H), and 6.53 (s, 1H)].

Tricyclo[4.4.0.$1^{7,10}$]undec-8-ene-2,5-dione monoethylene ketal (45)

This compound was synthesized in a similar manner to that reported for its 4-phenyl derivative (70). Thus, a solution of tricyclo[4.4.1.$0^{7,10}$]undec-8-ene-2,5-dione (44) (70) (65.8 g, 0.37 mol), ethylene glycol (23.0 g, 0.37 mol), and 0.1 g *p*-toluenesulfonic acid in 300 ml of benzene was heated to reflux for 23 hr with stirring. The water was collected in a Dean-Stark trap. The solution was cooled, washed with saturated $NaHCO_3$, saturated NaCl, and dried. Removal of solvent *in vacuo* gave 73.0 gm (90%) of a yellow oil. Crystallization from ethyl acetate-hexane afforded 45 (58.9 g, 0.37 mol, 72%) as fine white needles: mp 61.3-62.0°; pmr ($CDCl_3$) δ 1.34 (m, 2H), 1.51-2.68 (m, 4H), 2.74-3.20 (m, 2H), 3.33 (m, 2H), 4.00 (s, 4H), and 6.12 (t, 2H, J = 1.5 Hz); ir ($CHCl_3$) 1709 (C=O), 1452, 1343, and 1122 cm^{-1} (C-O-C); mass spectrum (70 eV) *m/e* (relative intensity) M^+ = 220 (12), 155 (13), 126 (31), 99 (46), and 66 (100).

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.89%; H, 7.32%;
Found: C, 70.91%; H, 7.32%.

Cyclohex-2-ene-1,4-dione monoethylene ketal (46)

This compound was synthesized in a manner similar to that reported (70) for its 5-methyl and 5-phenyl derivatives. Tricyclo[4.4.0.$1^{7,10}$]undec-8-ene-2,5-dione monoethylene ketal (45) (15.1 g, 0.069 mol) was rapidly distilled twice at 25

Torr with the pot temperature at 200° through a 2.5 inch insulated column packed with glass helices to give the desired product (6.15 g, 0.040 mol, 58%) as a colorless oil: bp 141-150° (20 Torr).

An analytical sample was obtained by preparative glpc (0.25 in x 5 ft, 15% XF 1150, 150°, 80 cm^3/min flow): pmr ($CDCl_3$) δ 1.71-3.05 (sym m, 4H), 3.93 (s, 4H), and 5.88 (d, 1H, J = 10.5 Hz), and 6.56 (d, 1H, J = 10.5 Hz); mass spectrum (70 eV) *m/e* (relative intensity) M^+ = 154 (6), 126 (100), and 110 (28).

Anal. Calcd. for $C_{10}H_{12}O_3$: C, 66.65%; H, 6.71%;
Found: C, 66.49%; H, 6.67%.

7,8-Dichlorobicyclo[4.2.0]octane-2,5-dione monoethylene ketal (47)

A magnetically stirred solution of 3.75 g (0.0244 mol) of 46 in 250 ml of dichloroethylene in a Pyrex immersion well apparatus fitted with a condenser was irradiated with a 450 W Hanovia lamp under a slow nitrogen flow. After 3 hr pmr analysis indicated all of the starting material had been consumed. Removal of the excess dichloroethylene *in vacuo* gave greater than quantitative recovery (6.51 g, 0.026 mol, 106%) of a light brown oil (pmr ($CDCl_3$) δ 1.92-2.74 (m, 4H), 3.26-3.44 (m, 2H), 3.87-4.16 (m, 4H), and 4.25-4.84 (m, 2H) which was used without purification in the next step.

Bicyclo[4.2.0]oct-7-ene-2,5-dione monoethylene ketal (48)

From dichloride 47 A stirred solution of 12.34 g (0.0492 mol) of the crude dichloride 47, 19.3 g (0.295 mol) of zinc dust, and 6.71 g (0.0492 mol) of $ZnCl_2$ in 150 ml of 95% ethanol was heated at reflux for 6 hr and then stirred at room temperature for 3 hr. The unreacted zinc was removed by filtration and washed with 150 ml of ether. The filtrate was diluted with 350 ml of saturated NaCl and the resulting organic phase separated. The aqueous layer was extracted with 100 ml of ether. The combined ether extracts were washed with 100 ml of water, 100 ml of saturated NaCl, dried, and filtered. The ether solution was treated with charcoal, filtered, and the solvent removed *in vacuo* to give a light yellow oil. Column chromatography on silica gel (ethyl acetate-$CHCl_3$, 5:95) gave 5.82 g (0.0323 mol, 66%) of a light yellow oil: bp 104° (0.6 Torr).

An analytical sample was obtained by preparative glpc (0.25 in x 6 ft, 20% SE-30, 160°, 100 ml/min flow): pmr ($CDCl_3$) δ 1.43-2.70 (m with prominent doublet at 2.48, 4H), 3.05-3.30 (m, 1H), 3.43-3.56 (m, 1H), 4.03 (s, 4H), 6.10 (m, 1H), and 6.32 (m, 1H); ir ($CHCl_3$) 1709 (C=O), 1452, 1412, 1364, 1322, and 1118 cm^{-1} (C-O-C); mass spectrum (70 eV) *m/e* (relative intensity) M^+ = 180 (56), 99 (100), and 66 (63).

Anal. Calcd. for $C_{10}H_{12}O_3$: C, 66.65%; H, 6.71%;
Found: C, 66.49%; H, 6.67%.

From bisethylene ketal 51 A solution of bisethylene ketal 51 (0.335 g, 1.50 mmol) and pyruvic acid (0.331 g, 3.76 mmol) in 10 ml of CH_2Cl_2 was heated to reflux for 8 hr under N_2 and then stirred at room temperature overnight. Another 15 ml of CH_2Cl_2 was added and the reaction mixture was washed with saturated $NaHCO_3$ (2 x 25 ml), water (2 x 25 ml), dried, filtered and the solvent removed *in vacuo* to give 0.253 g (1.41 mmol, 94%) of a light yellow oil which was in all respects identical to monoethylene ketal 48 obtained by reduction of the dichloride 47.

Longer reaction times using a great excess of pyruvic acid or stirring with dioxane-5% H_2SO_4 (1:1) would not remove more than one protecting ketal function. Stirring with dioxane-5% H_2SO_4 (1:1) for 5 hr at reflux resulted in the recovery of tars.

Bicyclo[4.2.0]oct-7-ene-2,5-dione (49)

From the hydrolysis of ketal 48 A solution of 48 (0.50 g, 2.78 mmol) in 5 ml of dioxane containing 3 ml of 3% H_2SO_4 was stirred under N_2 for 24 hr. The solution was neutralized by addition of ≈4 ml of saturated $NaHCO_3$ and then saturated with NaCl. The aqueous solution was continuously extracted with ether for 48 hr. The ether extract was dried and the solvent removed *in vacuo* to give 0.35 g of a yellow oil. The pmr spectrum indicated the crude material to be

≈30% desired product and ≈70% starting material. The two materials were separated on a silica gel column (ethyl acetate-benzene, 20:80) to give 90 mg (0.66 mmol, 24%) of <u>49</u> and 210 mg of <u>48</u>.

<u>From the zinc reduction of bicyclo[4.2.0]octa-3,7-diene-2,5-dione (40)</u> A magnetically stirred suspension of zinc dust (1.06 g, 16.1 mmol) in 25 ml of 10% aqueous HOAc under N_2 in a 3-neck 100 ml round bottom flask with an addition funnel and condenser was heated to 90°. Enedione <u>40</u> (1.44 g, 10.8 mmol) was added in one portion and the mixture was stirred for 1.5 hr at 90° and then cooled to room temperature. Addition of ethyl acetate precipitated $Zn(OAc)_2$ as a flocculent white solid which was removed by filtration and washed with ethyl acetate. The combined filtrates were stripped of solvent on a rotary evaporator and the residue was treated with ethyl acetate. The ethyl acetate solution was dried, filtered, and the solvent removed <u>in vacuo</u> to give 1.317 g of an orange oil. Compound <u>49</u> was eluted from a silica gel column (ethyl acetate-$CHCl_3$, 1:3) to give 1.05 g (7.79 mmol, 72%) of a pale yellow oil. Dione <u>49</u> was appreciably water soluble.

An analytical sample was obtained by preparative glpc (0.25 in x 6 ft, 5% Carbowax on Chromosorb W, 160°, 90 ml/min flow): pmr ($CDCl_3$) δ 2.46-3.33 (sym m, 4H), 3.82 (s, 2H), and 6.36 (s, 2H); ir (film) 1712 (C=O), 1310, 1270, 1178, 819, 762, and 685 cm^{-1}; mass spectrum (70 eV) <u>m/e</u> (relative intensity) M^+ = 136 (26), 108 (42), 93 (27), 79 (100), and 63 (86).

High Resolution MS Calcd. for $C_8H_8O_2$: 136.052423;
Found: 136.052362.

Reaction of 49 with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)

A solution of ketal 49 (0.86 g, 5.6 mmol) and 1.33 g (5.9 mmol) of DDQ (Aldrich) in 80 ml of dioxane (freshly distilled from Na metal) was heated to reflux under N_2 for 42 hr. The dioxane was removed *in vacuo* and the residue was stirred with 25 ml of benzene and filtered to remove the hydroquinone of DDQ. Removal of solvent gave a brown mush.

The residue was passed through a column of neutral alumina (Act. I) eluting first with 1 ℓ of benzene and then 1.5 ℓ of $CHCl_3$. Removal of solvents *in vacuo* gave a dark oil. A pmr spectrum of this oil revealed no olefinic resonances (not even starting material).

7,8-Dichlorobicyclo[4.2.0]octane-2,5-dione bisethylene ketal (50)

A solution of 6.51 g (0.0259 mol) of 7,8-dichlorobicyclo[4.2.0]octane-2,5-dione monoethylene ketal (47), 2.50 g (0.040 mol) of ethylene glycol, and 20 mg of *p*-toluenesulfonic acid in benzene was heated to reflux for 27 hr. Water was collected in a Dean-Stark trap. The solution was cooled and washed with saturated $NaHCO_3$ (2 x 75 ml), 50 ml of saturated NaCl, dried and filtered. The solvent was removed *in vacuo* to give an off-white solid which was taken up in hot $CHCl_3$-Skelly B. An insoluble brown precipitate was removed by filtration. Removal of solvent yielded 6.81 g (0.0231 mol, 89%) of 50 as a clear oil which solidified upon standing: bp 113° (1.2 Torr); pmr ($CDCl_3$) δ 1.2-2.3 (br m, 4H), 2.95 (m, 1.3H), 3.90 (s, 8H), 4.53 (m, 1.3H), and 6.65 (m, 1.3H).

The pmr spectrum is consistent with a mixture of epimeric dichlorides.

Bicyclo[4.2.0]oct-7-ene-2,5-dione bisethylene ketal (51)

To a THF solution (100 ml, distilled from $LiAlH_4$) of naphthalene (2.87 g, 0.224 mol) in a flame-dried 250 ml 3-neck round bottom flask equipped with pressure equalizing addition funnel, N_2 atmosphere, and magnetic stirrer was added 0.52 g (0.023 g-atom) of Na metal cut into small pieces. After 5 min, the solution had turned dark green. After stirring at room temperature for 1.5 hr, the solution was cooled in an ice bath and dichloride 50 (2.18 g, 0.00739 mol) in 30 ml of dry THF was added over 45 min with the temperature maintained at 0-5°. The brownish-green solution was allowed to warm to room temperature and 2 ml of MeOH was added. Upon addition of the first drop of MeOH, the solution immediately turned bright yellow. The MeOH was followed by 20 ml of H_2O. The aqueous layer was separated from the THF layer and washed with pentane (2 x 20 ml). The combined organic phases were combined and dried. Filtration and removal of solvent *in vacuo* gave 5 g of a dark solid. The naphthalene was removed by chromatography on silica gel (CCl_4) and the column was then stripped with MeOH. Removal of solvent from the naphthalene-free fraction gave a dark oil which was distilled through a short-path apparatus to give 0.67 gm (0.00299 mol, 40%) of 51: bp 113° (1.2 Torr); pmr ($CDCl_3$) δ 1.43-2.24 (sym m, 4H), 3.03 (s, 2H), 3.86 (s, 8H), and 6.03 (s, 7H).

Attempts to reduce the vicinal dichloride 50 with $Zn/ZnCl_2$ in a manner similar to that described for dichloride 47 resulted in recovery of starting material after as much as 24 hrs at reflux.

Photochemical adduct (54) of benzoquinone-anthracene Diels-Alder adduct and dichloroethylene

A nitrogen deoxygenated solution (0.79 g, 2.80 mmol) of the Diels-Alder adduct 53 (108) in 90 ml of dichloroethylene in a Pyrex vessel with internal cooling was irradiated at 3600Å in a Rayonet Photochemical Reactor. After 5 hr, pmr analysis indicated that the starting material, 52, had been consumed. Removal of solvent *in vacuo* gave 1.03 g (2.72 mmol, 97% crude) of an orange-brown oil. The pmr spectrum showed complex resonances (($CDCl_3$) δ 2.5-3.7, 4.5-5.1, and 6.8-7.6) fairly consistent with the expected product. This material was used directly without purification in the next step.

Reaction of crude dichloride 54 with Zn

The crude dichloride 54 (1.03 g, 2.71 mmol) obtained by the photochemical addition of dichloroethylene and the Diels-Alder adduct of benzoquinone with anthracene was dissolved in 250 ml of 95% EtOH containing 1.07 g (16.3 mmol) of Zn dust and 0.37 g (2.71 mmol) of $ZnCl_2$. The solution was heated to reflux under N_2 for 6 hr. The solution was cooled, filtered to remove the Zn, and concentrated to one-half volume *in vacuo*. The ethanolic solution (~125 ml) was diluted with 500 ml of water and extracted with CH_2Cl_2 (2 x 250 ml). The combined CH_2Cl_2 extracts were washed with saturated $NaHCO_3$ (2 x 250 ml), water (1 x 250 ml), saturated NaCl (1 x 250 ml), and dried. Filtration and removal of solvent gave a dark orange oil. The pmr of this oil did not show the expected olefinic resonances of 55, but did exhibit a much more complex spectrum than the crude starting material 54. This route was subsequently abandoned.

trans-7,8-Dibromobicyclo[4.2.0]octa-2,4-diene (56)

This compound was prepared by the addition of Br_2 to cyclooctatetraene as described in the literature by Reppe and coworkers (29). The dibromide was obtained in 64% yield by distillation of the crude reaction product: bp 85-86° (0.30 Torr) [Lit. (29) bp 90-91° (1 Torr)].

It was found that elution of the crude reaction material through a pad of silica gel using CH_2Cl_2 with suction gave higher yields (90%), was more convenient, and gave material of comparable purity to that obtained by distillation.

trans-3,4-Dibromo-9,10-dioxytricyclo[4.2.2.0^{2,5}]deca-7-ene (57)

The preparation of this compound was performed using the general procedure for addition of singlet oxygen to dienes. Thus, irradiation of the dibromide 56 (14.47 g, 0.0548 mol) for 6 hr in 1000 ml of reagent grade acetone using hematoporphyrin as a sensitizer gave, after removal of solvent and elution through a pad of silica gel with benzene, 14.79 g (0.0500 mol, 91%) of epidioxide 57 as a white solid. Recrystallization of a small portion of this material from ether gave 57 as colorless prisms: mp 104-106°; pmr ($CDCl_3$) δ 3.57 (m, 2H), 4.18 (m, 1H), 4.74 (m, 3H), 6.73 (ddd, J = 8, 6, 2 Hz), and 7.12 (ddd, J = 8, 6, 2 Hz) [Lit. (72) mp 106-107°; pmr ($CDCl_3$) δ 3.60 (m, 2H), 4.24 (m, 1H), 4.80 (m, 3H), 6.69 (ddd, J = 8.0, 6.0, 2.0 Hz), and 7.10 (ddd, J = 8.0, 6.0, 2.0 Hz)].

trans-7,8-Dibromobicyclo[4.2.0]octa-3-ene-2,5-diol (58)

To a magnetically stirred suspension of $LiAlH_4$ (0.55 g, 14.6 mmol) in 30 ml of THF (distilled from $LiAlH_4$) under N_2

in a flame-dried 250 ml 3-neck flask equipped with an addition funnel was added over 45 min at room temperature a solution of the epidioxide 57 (2.88 g, 9.73 mmol) in 40 ml of dry THF. Addition of each drop of solution caused vigorous bubbling. Workup was accomplished using the method suggested by Fieser and Fieser (109) (for each n grams of $LiAlH_4$ add successively n grams H_2O, n grams 15% NaOH, 3n grams H_2O). The resulting solid was suction filtered with the aid of Celite to prevent clogging of the filter and the filtrate was washed with additional THF.

The filter cake was stirred in hot THF and again suction filtered. The combined THF filtrates were combined, dried, filtered, and the solvent was removed to give 2.58 g (8.66 mmol, 89%) of the diol 58. Recrystallization from $CHCl_3$ gave the compound as white prisms: mp 129.5-131.0° [Lit. (72) mp 135-136°].

Due to its limited solubility in convenient pmr solvents, a pmr spectrum was not obtained.

trans-7,8-Dibromo-2,5-diacetoxybicyclo[4.2.0]oct-3-ene (59)

A suspension of diol 58 (2.58 g, 8.66 mmol), freshly distilled acetic anhydride (5.0 g, 49 mmol), and 0.5 ml of pyridine in 150 ml of benzene was heated to reflux under N_2. After 2 hr the initially cloudy solution was clear. The mixture was cooled and washed with water (2 x 100 ml), saturated $NaHCO_3$ (2 x 100 ml), and dried. Removal of solvent gave a faint yellow syrup. Elution through a pad of silica gel with benzene aided by suction gave 3.12 g (8.17 mmol, 94%) of 59 as an off-white solid: pmr ($CDCl_3$) δ 2.05 (s, 6H), 2.98 (m, 2H), 4.26 (d, 1H, J = 7.5 Hz), 4.57 (br d, 1H, J = 7.5 Hz), 5.08 (m, 1H), 5.44 (m, 1H), and 5.94 (m, 2H) [Lit. (72) pmr ($CDCl_3$) δ 2.09 (s, 6H), 3.00 (m, 2H), 4.30 (d, 1H, J = 7.5 Hz), 4.63 (dd, 1H, J = 7.5, 1.2 Hz), 5.15 (m, 1H), 5.54 (m, 1H), and 6.05 (m, 2H)].

2,5-Diacetoxybicyclo[4.2.0]octa-3,7-diene (60)

A suspension of 6.08 g (15.9 mmol) of dibromide 59, 5.2 g (79.5 mmol) of Zn dust, and a small crystal of iodine in 40 ml of dry DMSO (distilled from CaH_2) was heated to 90° for 3.5 hr under N_2. The reaction mixture was cooled and suction filtered through a pad of Celite. The Celite pad was washed with another 25 ml of DMSO. The DMSO filtrates were combined and the DMSO was removed by vacuum distillation (35°, 0.1 Torr). The residue was dissolved in 100 ml of ethyl acetate and washed with water (2 x 75 ml), saturated $NaHCO_3$ (1 x 75 ml), saturated NaCl (1 x 75 ml) and dried. Filtration and removal of solvent gave 3.18 g (14.31 mmol, 90%) of diacetate 60 as a faint yellow, very viscous syrup which slowly crystallized at room temperature to form colorless prisms: pmr ($CDCl_3$) δ 2.07 (s, 6H), 3.11 (br s, 2H), 5.21 (br s, 2H), 5.94 (dd, 2H, J = 3.0, 1.5 Hz), and

6.03 (s, 2H) [Lit. (72) pmr ($CDCl_3$) δ 2.00 (s, 2H), 3.02 (narrow m, 2H), 5.10 (m, 2H), 5.96 (dd, 2H, J = 2.8, 1.0 Hz), and 6.13 (s, 2H)].

Bicyclo[4.2.0]octa-3,7-diene-2,5-diol (61)

To a magnetically stirred suspension of 0.76 g (20 mmol) of $LiAH_4$ in 30 ml of THF (distilled from $LiAlH_4$) under N_2 in a flame-dried 250 ml 3-neck flask equipped with a condenser and addition funnel was added 3.67 (16.5 mmol) of diacetate 60 in 40 ml of dry THF over 45 min. The solution was stirred at reflux for 1.5 hr and cooled. Workup by the method of Fieser and Fieser (109), filtration through Celite, and removal of solvent *in vacuo* gave a near quantitative yield of the crude diol 61 as a colorless oil which showed no extraneous resonances in the pmr spectrum. The oil was eluted through a silica gel column (ether-$CHCl_3$, 15:85) to give 1.51 g (10.9 mmol, 66%) of 61: pmr ($CDCl_3$) δ 3.15 (s, 2H), 3.22 (s, 4H), and 5.98 (s, 4H); ir (film) 3330 (strong, broad, O-H), 1427, 1283, 792, 734, and 713 cm^{-1} [Lit. (72) pmr ($CDCl_3$) δ 3.22 (s, 2H), 3.45 (br s, (OH), 2H), 4.25 (m, 2H), and 6.10 (narrow m, 4H); ir (film) 3300, 1640, 1560, 798, 738, and 718 cm^{-1}].

On occasion, workup using the described method gave the diol 61 as a 1:1 THF complex: pmr ($CDCl_3$) δ 1.56 (m, 4H), 3.08 (br s, 2H), 3.54 (m, 4H), 4.15 (br s, 2H), 4.50 (br s, 2H), 5.94 (m, 2H), and 5.98 (s, 2H). The resonances at

1.56 and 3.54 were nearly identical in shape (but shifted upfield somewhat) to those of THF itself (δ = 1.85, and 3.75). The THF was not removed by chromatography on silica gel nor by heating under high vacuum. The oxidation of the diol to the diketone was not affected, however.

Bicyclo[4.2.0]oct-3,7-diene-2,5-dione (40)

From Cr^{+6} oxidation of diol 61 To a stirred solution of 0.40 g (2.9 mmol, 11.6 meq) of diol 61 in 25 ml of reagent grade acetone cooled in an ice bath was added 1.45 ml of a 2.67 M solution (11.6 meq) of Jones' reagent (110) (prepared by dissolving 2.67 g of CrO_3 in 2.3 ml of concentrated H_2SO_4 and dilution to 10 ml with H_2O) dropwise over 10 minutes. The precipitation of green chromous salts was immediate upon addition of each drop. The reaction mixture was stirred an additional 5 min at 0°, then diluted with 150 ml of H_2O. The aqueous solution was extracted with ether (3 x 50 ml). The combined ether extracts were washed with water (2 x 50 ml), saturated $NaHCO_3$ (2 x 25 ml), saturated NaCl (1 x 50 ml), and dried. Removal of solvent gave 0.28 g (72% crude) of a yellow oil.

Elution from a column of neutral alumina (Activity I) with CH_2Cl_2 gave 0.183 g (1.36 mmol, 47%) of dione 40 as a yellow oil which solidified as yellow plates upon standing: mp 44-46°; pmr ($CDCl_3$) δ 3.95 (s, 2H), 6.37 (s, 2H), and

6.67 (2, 2H); ir ($CHCl_3$) 1679 (C=O), 1604 (C=C), 1560, and 962 cm^{-1} [Lit. (72) mp 51-52°; pmr ($CDCl_3$) δ 3.92 (s, 2H), 6.37 (s, 2H), and 6.65 (s, 2H); ir (KBr) 1675, 1603, 1560, and 962 cm^{-1}].

An analytical sample, which was also used for the esr experiments, was obtained by glpc (0.25 in x 6 ft, 20% SE-30, 135°, 80 ml/min flow rate).

Anal. Calcd. for $C_8H_6O_2$: C, 71.63%; H, 4.52%;
Found: C, 71.57%; H, 4.60%.

From MnO_2 oxidation of diol 61 A suspension of 15 g (174 mmol) of activated MnO_2 (prepared by the method of Mancera and coworkers (111)) and 0.754 g (5.46 mmol) of diol 61 in 100 ml of $CHCl_3$ was stirred under N_2 for 30 hr. The suspension was filtered and the solids washed with ethyl acetate. Removal of solvents *in vacuo* gave 0.493 g (3.68 mmol, 67%) of dione 41 essentially pure by pmr.

1α,2α,3α,8α-4,5,10,11-Tetramethyltricyclo[$6.4.0.0^{2,7}$]dodeca-4,10-diene-3,6,9,12-tetraone (80)

This compound was prepared in a manner similar to that reported by Cookson and coworkers (112). Crystalline 2,3-dimethyl-1,4-benzoquinone (0.50 g, 3.7 mmol) in a watch glass was exposed to sunlight (mid-December, Ames, Iowa) for 4.5 hr after which time the initially bright yellow solid had turned tan. The solid was treated with 100 ml of boiling ether and an insoluble creamy-white solid was removed by filtration. More of this solid precipitated out of solution after the solution had stood overnight. This, too, was removed by filtration. The residue was placed on a silica gel column and elution with benzene gave as the first fraction off the column unreacted 2,3-dimethyl-1,4-benzoquinone. Tetraone 80 was obtained as the second fraction upon elution with ethyl acetate-benzene (10:90). Recrystallization from ether afforded 0.055 g (.20 mmol, 11%) of 80 as pale yellow plates: mp 161-163° [Lit. (14) 163-164°], pmr ($CDCl_3$) δ 1.86 (s, 6H), and 3.83 (s, 2H).

2,4-Cyclooctadiene-1,6-dione (84)

This compound was prepared by the procedure outlined by Oda and coworkers (83). Thus, flash thermolysis of 201.3 mg (1.480 mmol) of bicyclo[4.2.0]octa-7-ene-2,5-dione (49) at 500 ± 10°C at 0.03 Torr through a 2.2 cm x 32 cm quartz tube packed with quartz chips gave 176.6 mg (1.299 mmol, 87.7% crude) of a bright yellow liquid which condensed before reaching the cooled (liquid nitrogen) trap. The literature (83) reports no purification procedure for 84. Purification by microdistillation at 75° (0.1 Torr) gave 84 as a faint yellow liquid. Some orange residue remained in the pot. Other than the previously cited failure to produce well resolved esr signals, the spectral properties of the crude pyrolysate were identical to those of the purified material:

pmr ($CDCl_3$) δ 2.84 (s, 4H), 6.09 (dt, 2H, J = 12.5, 2.5 Hz), and 6.52 (dt, 2H, J = 12.5, 2.5 Hz), small impurity peaks at δ 2.74 (d), and 3.3 (m); mass spectrum (16 eV) m/e (relative intensity) M^+ = 136 (30), 108 (100), 94 (94), 80 (28), and 66 (52) [Lit. (83) pmr ($CDCl_3$) δ 2.79 (s, 4H), 6.02 (dt, 2H, J = 13.2, 2.0 Hz), and 6.39 (dt, 2H, J = 13.2, 2.0 Hz)].

Preparative thin layer chromatography (≈40 mg per plate, 0.6 mm x 20 cm x 20 cm, Silica Gel PF-254, Merck) using ether-benzene (45:55) resulted in the appearance of a brown smear behind the band identified as diene-dione 84. The recovery of dione 84 from material that was reasonably pure to begin with was only 33%. In addition, this purification technique did not remove the impurity peaks present in the pmr of the crude pyrolysate. The results of preparative thin layer chromatography on alumina (Merck PF 254 + 356) were similar.

2,5,7-Cyclooctatriene-1,4-dione (85)

This compound was prepared by the method outlined by Oda and coworkers (83). To a solution of the crude pyrolysate (compound 84) from the flash thermolysis of 304.8 mg (2.239 mmol) of bicyclic dione 49 in 6 ml of 1:2 CF_3CO_2H-CH_3Cl_2 (CF_3CO_2H was distilled; CH_2Cl_2 was distilled and stored over 4H sieves) was added 0.3922 g (2.203 mmol) of N-bromosuccinimide (NBS). The solution was stirred under N_2 for 1 hr at room temperature during which time the initially light orange solution turned light brown. The solution was then cooled in an ice bath and 4.0 ml of Et_3N (distilled) was added over 2 min. Addition of the first 0.5 ml of the amine was accompanied by evolution of dense white fumes. The solution was stirred at room temperature for 5 min. The solvent was removed *in vacuo* to give ≈10 ml of a reddish-brown slush. This residue was eluted from a column of 150 g of silica gel (ethyl acetate-$CHCl_3$, 5:95) to give 120.1 mg (0.896 mmol) of crude dione 85 as the first fraction (estimated purity 80%, ≈32% yield before purification).

Preparative glpc (0.25 in x 6 ft DC-550, 150°, 100 ml/min flow rate) gave triene-dione 85 as a light yellow solid which melted slightly above room temperature: pmr ($CDCl_3$) δ 6.03 (dt, 2H, J = 14, 2 Hz), 6.43 (dt, 2H, J = 14, 2 Hz), and 6.66 (s, 2H); ir ($CHCl_3$) 1665 (br, C=O), 1616, 1489, 1409, and 1128 cm^{-1}; mass spectrum (70 eV) *m/e* (relative intensity) M^+ = 134 (22), 106 (18), 78 (100), and 52 (64) [Lit. (83) yellow liquid; pmr ($CDCl_3$) δ 6.00 (dt, 2H, J = 13.5, 2.0 Hz), 6.40 (dt, 2H, 13.5, 2.0 Hz), and 6.61 (s, 2H); ir (film) 1650 (broad), 1610, and 1125 cm^{-1}; mass spectrum *m/e* M^+ = 134, 106, and 78].

High resolution mass spectrum: Calcd. for $C_8H_6O_2$: 134.03678; Found: 134.03711.

1,6-Dibromo-2,4-cyclooctadiene (102)

This compound was prepared by the reaction of 1,5-cyclooctadiene with NBS with benzoyl peroxide as the catalyst as described by Cope and coworkers (113). The crude product could be purified by distillation from $CaCO_3$ (bp 109-111° 1.7 Torr) [Lit. (113) bp 95-105° (1 Torr)]; however, this always led to darkening of the initially golden-yellow liquid in the receiver. Dibromide 102 was more conveniently purified by eluting the crude reaction product from a silica gel column with CCl_4 to give 102 as a yellow liquid in over 90% yield: pmr ($CDCl_3$) δ 1.7-3.8 (br m, 4H), 4.05-5.25 (m, 2H), and 5.30-6.50 (m, 4H).

6-Bromo-2,4-cyclooctadiene-1-one (103)

A suspension of 27.0 g (0.32 mol) of $NaHCO_3$ and 42.2 g (0.158 mol) of dibromide 102 in 150 ml of DMSO (distilled from CaH_2) was stirred for 8 hr at room temperature. Moisture was excluded by a $CaCl_2$ drying tube. The reaction mixture was diluted with 300 ml of water and extracted with ether (2 x 250 ml). The combined ether extracts were washed with water (5 x 250 ml), saturated NaCl (1 x 250 ml), and dried over Na_2SO_4. The ether solution was filtered and the solvent was removed *in vacuo* to give 26.7 g (0.133 mol, 84%) of the crude bromo ketone 103 which was reasonably pure by pmr. Distillation was accompanied a great deal of decomposition and the distillate slowly turned dark green in the receiver.

Elution from a column of silica gel (ethyl acetate-benzene, 5:95) gave 103 as a yellow oil: pmr ($CDCl_3$) δ 2.05-3.10 (m, 4H), 4.25-4.93 (m, 1H), and 5.45-6.75 (m, 4H);

ir (film) 1662 (C=O), 1603 (C=C), 1169, and 1146 cm^{-1}; mass spectrum (70 eV) m/e (relative intensity) $M^{+}(^{79}Br)$ = 200 (10), 158 (26), 121 (30), and 79 (100).

High Resolution Mass Spectrum: Calcd. for C_8H_9OBr: 199.9837; Found: 199.9838.

In an attempt to favor oxidation over elimination, the reaction was performed using hindered bases (collidine, lutidine, etc.), higher temperatures (55-100°), and $AgClO_4$ used in various combinations. These variations have been shown to be effective for the oxidation of secondary halides to ketones (114). However, in all cases analysis of the crude reaction product (tlc and pmr) indicated complex mixtures and absence of starting material. Cyclooctatriene-one (104) could be identified in some of the pmr spectra by its characteristic resonance at δ = 2.95 (d, J = 8 Hz).[6] At no time was the presence of 2,4-cyclooctadiene-1,6-dione (84) indicated.

6-Acetoxy-2,4-cyclooctadiene-1-one (106)

A solution of 0.55 g (2.8 mmol) of bromo ketone 103 and 1.72 g (13 mmol) of tetramethylammonium acetate in 50 ml of reagent grade acetone was stirred at reflux under N_2 for 23 hr.

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[6] Private communication, E. J. Goettert, Iowa State University, Ames, Iowa, 1973.

The solution was cooled and diluted with 25 ml of water. The aqueous solution was extracted with ether (2 x 75 ml). The combined ethereal extracts were washed with 10% K_2CO_3 (1 x 50 ml), water (2 x 50 ml), saturated NaCl (1 x 50 ml), and dried over Na_2SO_4. The ether solution was filtered and the solvent removed to give 0.30 g of a brown oil. This oil was eluted from a column of silica gel (ethyl acetate-Skelly B, 45:55) to give 0.16 g (0.89 mmol, 31%) of 106 as a light yellow oil. An analytical sample was obtained by preparative glpc (0.375 in x 10 ft, 5% Carbowax 20M, 165°, 120 ml/min flow rate): pmr ($CDCl_3$) δ 1.2-2.7 (series of sharp multiplets, 4H), 2.04 (s, 3H), 5.6-6.8 (m, 5H); mass spectrum (70 eV) *m/e* (relative intensity) M^+ = 180 (not observed), 120 (44.5), 91 (100), 65 (26), and 50 (17.5).

Anal. Calcd. for $C_{10}H_{12}O_3$: C, 66.65%; H, 6.71%;
Found: C, 64.95; H, 6.13%.

Although the C,H analysis was not within acceptable limits, the spectral data was consistent with the presence of 106 in reasonable purity and the sample was used for esr experiments.

AIBN catalyzed reaction of Cyclooctatraene with oxygen

Continuous bubbling of oxygen into a mixture of 2.08 g (20 mmol) of distilled cyclooctatetraene (Aldrich) and 93 mg (4.5% by weight) of azobisisobutyronitrile (AIBN) heated to

55-60° for 17 hr gave a red, tarry material which gave only weak esr signals in normal static esr experiments.

When the experiment was repeated using chlorobenzene as a solvent, the final product was again a red tar, but the reaction was much slower. It took nearly 4 days to obtain the gooey residue obtained in the experiment performed without solvent.

Reaction of cyclooctatetraene with singlet oxygen

A solution of 1.0 g (9.6 mmol) of cyclooctatetraene in absolute ethanol containing 60 mgm of hematoporphyrin as a sensitizer was irradiated in the apparatus described in the general procedure. After 138 hr irradiation was halted. The solvent was removed to give a dark brown oil with a very sharp smell (not unlike acetic acid). The pmr spectrum was dominated by a broad, intense resonance in the aromatic region ($\delta = 7.6$). This resonance was not at all consistent with the desired epidioxide. Nevertheless, the crude oil was stirred with a small amount of silica gel in benzene to remove sensitizer and filtered. After removal of solvent, the residue was dissolved in 2 ml of 95% EtOH. The ethanolic solution was cooled in an ice bath, 1.5 ml of triethylamine was added, and the solution was allowed to warm to room temperature over 2 hr. The solvent was removed *in vacuo* to give a dark brown oil which was used for the esr experiment described in the Discussion.

The reaction of cyclooctatetraeneirontricarbonyl (108) with singlet oxygen

A solution of 1.20 g (4.92 mmol) of cyclooctatetraeneirontricarbonyl (108)[7] and 10 mg of hematoporphyrin in 250 ml of reagent grade acetone was irradiated according to the general procedure for singlet oxygen addition. After 6 days, no oxygen uptake had been noted. A small amount of a brown film had been deposited on the glass at the surface of the solution. Removal of solvent gave a red solid which by pmr was solely unreacted starting material.

Generation of bis-1,4-cyclooctatetraenemagnesium bromide (109) and its reaction with t-butylperoxymagnesium bromide

A flame-dried 50 ml 3-neck flask equipped with a condenser, magnetic stirring bar, septum, and a N_2 atmosphere was charged with 0.27 g (11 g-atom) of Mg turnings and 10 ml of THF (distilled from $LiAlH_4$). 1.31 g (5.00 mmol) of 1,4-dibromocyclooctatetraene (115) in 15 ml of anhydrous THF was added and the solution was heated to reflux. A tan precipitate was evident soon thereafter. After 3 hr at reflux a great deal of Mg remained. A small crystal of iodine was added and reflux was continued for 12 hr. The resulting orange solution

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[7] Supplied by Dr. T. J. Barton, Iowa State University, Ames, Iowa.

had precipitated a great deal of a fine, light-colored solid. A small amount of the suspension, withdrawn by syringe, turned orange immediately upon contact with air and reacted vigorously with water. The suspension was cooled to room temperature and added dropwise *via* syringe over 20 min to a -60° solution of *t*-BuOOMgBr (prepared by the addition of 4.1 ml (11.5 mmol) of a 2.81 M ethereal solution of CH_3MgBr (Ventron) to 0.99 g (11 mmol) of *t*-BuOOH in 10 ml of THF at -60°).

The stirred solution was allowed to warm to room temperature over 2.5 hr. The reaction mixture was neutralized with 5% HCl and extracted with ether (2 x 75 ml). The combined ether extracts were washed with water (100 ml), saturated $NaHCO_3$ (100 ml), saturated NaCl (100 ml), and dried. Removal of solvent *in vacuo* gave 0.70 g (103% of theoretical) of an orange oil. The crude oil was eluted on a column of silica gel (dry column technique) (ethyl acetate-hexane, 15:85). The first fraction eluted was the major fraction. The pmr spectrum showed a broad aromatic peak ($\delta = 7.2$) as the only significant resonance. The ir spectrum displayed a carbonyl absorption (1707 cm^{-1}). Since the pmr was not in accord with the desired compound, the route was abandoned.

Reaction of cyclooctatetraene epoxide (110) with *m*-chloroperbenzoic acid (MCPBA)

This reaction was performed following the procedure of Anastassiou and Reichmanis (94). A solution of 97 g (48 mmol) of 85% MCPBA (Aldrich) in 125 ml of CH_2Cl_2 was added to a stirred solution of 2.9 g (24 mmol) of cyclooctatetraene oxide (116) under N_2 over a period of 1 hr. The reaction was stirred at room temperature for 18 hr. The reaction mixture was washed with 100 ml of water and the aqueous wash was back-extracted with 150 ml of ether. The combined organic phases were washed with 10% NaOH (2 x 75 ml), water (1 x 100 ml), and dried over Na_2CO_3. Evaporation of solvent gave 3.26 g (100% of theoretical) of a faint yellow oil.

The crude product was eluted from a jacketed column of neutral alumina (Woelm, Act. II) at -15° with ether-Skelly B (≈250 ml of 10:90, then 400 ml of 25:75) taking 50 ml fractions. The first major component was a mixture of at least three compounds. Pmr indicated that all three of the diepoxides (111, 112, and 113) were present. Later eluting fractions were also mixtures of the three diepoxides. This separation was not nearly as efficient as the literature had suggested. Upon standing, the first fraction (solvent removed) began precipitating a white solid. The material was stored in a refrigerator for 4 days after which time more solid had precipitated. The solid was filtered off and washed with hexane to give 0.64 g (20%) of diepoxide <u>112</u> as white crystals: mp 153.0-155°; pmr ($CDCl_3$) δ 3.64 (s, 4H), and 5.74 (s, 4H); mass spectrum (70 eV) *m/e* (relative intensity) M^+ = 136 (22), 107 (100), 91 (43), 79 (80), and 77 (79) [Lit. (94) mp 165.5-166.5; pmr ($CDCl_3$) δ 3.67 (s, 4H), and 5.80 (s, 4H)].

The filtrate from the isolation of <u>113</u> appeared to be a mixture (by pmr) of all three diepoxides along with small amounts of unidentified material.

9,10-Dioxybicyclo[4.2.2]deca-7-ene (114)

This compound was prepared using the general procedure for singlet oxygen addition. Irradiation of 21.6 g (0.20 mol) of 1,3-cyclooctadiene (COD) in 1 ℓ of reagent grade acetone containing 200 mg of hematoporphyrin (added in small portions at 1 day intervals) for 1 week resulted in the uptake of 3.9 ℓ of oxygen (87% of theoretical). The solvent and excess COD was removed *in vacuo* to give a red oil which was suction filtered through a pad of silica gel with $CHCl_3$ washing (≈1 ℓ) to give after removal of solvent 18 g (0.13 mol, 65%) of a colorless oil which slowly solidified at room temperature: pmr ($CDCl_3$) δ 1.3-2.3 (m, 8H), 4.7 (m, 2H), and 6.12 (dd, 2H, J = 3.5, 2.0 Hz) [Lit. (94) pmr ($CDCl_3$) δ 1.4-2.3 (m, 8H), 4.06 (br s, 2H), and 6.05 (dd, 2H, J = 3.6, 2.0 Hz)].

1-Hydroxy-9-oxabicyclo[4.2.1]non-7-ene (115)

A solution of 4.4 g (31.4 mmol) of epidioxide 114, and 0.75 ml of triethylamine in 150 ml of CH_2Cl_2 was heated to reflux for 14 hr under N_2. The solution was cooled and the solvent and triethylamine were removed *in vacuo* to give a light tan solid with a very pungent smell. The crude material was eluted from a column of alumina (175 g, Act. I).with $CHCl_3$. The desired compound was preceded by a fast moving brown liquid. The hemiketal 115, 3.17 g (22.6 mmol, 72%), was obtained as fine, white needles when the eluant was concentrated: mp 92.0-92.8° [Lit. (116), mp 92-93°]; pmr ($CDCl_3$) δ 1.55 (br s, 4H), 1.89 (br s, 4H), 4.09 (s, 1H), 4.92 (br d, 1H, J = 5.8 Hz), 5.74 (dd, 1H, J = 5.9, 1.2 Hz), and 5.96 (dd, 1H, J = 5.9, 1.2 Hz).

2-Cyclooctene-1,4-dione (116)

A suspension of 2.80 g (20 mmol) of hemiketal 115 and 2.00 g (20 mmol) of CrO_3 in 100 ml of reagent grade acetone was stirred at room temperature for two days. The mixture was filtered through sintered glass and the black residue was washed with CH_2Cl_2. The solvents were removed from the filtrate *in vacuo* to give 2.69 g of a light yellow oil which was eluted from a column of silica gel (ethyl acetate-$CHCl_3$, 5:95). The first compound eluted was the desired ene-dione 116 (1.02 g, 7.39 mmol) followed by unreacted hemiketal (1.69 g, 12.09 mmol). The yield based on unrecovered starting material was 93%. Ene-dione 116 eluted from silica gel was a faint yellow oil at room temperature but solidified as a white solid in the refrigerator: pmr ($CDCl_3$) δ 1.90 (m, 4H), 2.58 (m, 4H), and 6.40 (s, 2H); ir ($CHCl_3$) 2950, 1679 (C=O), 1613 (C=C), 1456, 1097, and 906 cm^{-1}; mass spectrum (70 eV) m/e (relative intensity) M^+ = 138 (100), 100 (29), 94 (33), and 82 (87) [Lit. (95) mp 36.5-37.5°; pmr ($CDCl_3$) δ 1.90 (m, 4H), 2.52 (m, 4H), and 6.33 (s, 2H); ir (KBr) 1672, and 1611 cm^{-1}].

Anal. Calcd. for $C_8H_{10}O_2$: C, 69.54%, H, 7.30%;
Found: C, 69.37%; H, 7.53%.

Attempts to alpha-brominate 2-cyclooctene-1,4-dione (116)

Bromination with $CuBr_2$ A suspension of 0.24 g (1.74 mmol) of 2-cyclooctene-1,4-dione (116) and 1.55 g (6.94 mmol, theoretically one equivalent) of $CuBr_2$ in 20 ml of 1:1 ethyl acetate-$CHCl_3$ was heated to reflux under N_2 for 5 hr. The initially deep green suspension was bright green and contained a white precipitate after 1.5 hr. After 5 hr at reflux, the solution was light brown (an indication of complete reaction (96)). The solution was filtered and a light gray precipitate was removed by filtration. The dark brown organic filtrate was washed with water until neutral and dried. Filtration and removal of solvent gave 0.5 g (>100% crude) of a brown oil. Treatment with charcoal in

$CHCl_3$ gave a light orange oil after filtration and solvent evaporation. The pmr spectrum of this oil indicated significant aromatic resonances and extremely broad and intense resonances in the alkyl region (δ .8-2.9). The characteristic singlet of the olefinic protons of <u>116</u> had been replaced by a series of sharp resonances in the same region. Some "hash" appeared between 4.0 and 5.2 ppm which could have been the hydrogens on a brominated alpha carbon. In spite of the apparent failure of the reaction, the crude material was treated with Li_2CO_3-LiCl in DMF (117) in an attempt to dehydrohalogenate. A white vapor formed immediately upon contact of the crude product with DMF (30 ml, distilled from CaH_2). 1.5 g of Li_2CO_3 and 1.5 g of LiCl were added and the suspension was stirred at 75° for 4 hr. The suspension was cooled, diluted with 125 ml of water, and extracted with $CHCl_3$ (3 x 50 ml). The combined $CHCl_3$ extracts were washed with water (2 x 100 ml), saturated NaCl (1 x 100 ml), and dried. Filtration and removal of solvent gave an orange oil, the pmr of which was void of any olefinic resonances.

It was thought that in the bromination step liberated HBr might be brominating the double bond after alpha-bromination had occurred. However, when the reaction was run under the same conditions in the presence of solid $NaHCO_3$, no significant changes in the course of the reaction were observed.

Bromination with 2-carboxyethyltriphenylphosphonium perbromide 2.44 g (4.25 mmol) of 2-carboxyethyltriphenylphosphonium perbromide (97) was added in one portion to a stirred solution of 0.30 g (2.2 mmol) of 2-cyclooctene-1,4-dione 116 in THF (distilled from THF). Stirring at room temperature for 3 hr and at 55° for 1.5 hr did not affect discoloration of the initially orange solution. (According to the literature (97), the orange phosphonium perbromide should be converted to the insoluble white phosphonium bromide.) The solvent was removed *in vacuo* and the resulting orange slush was extracted with ether (2 x 50 ml). The combined colorless ether extracts were washed with water (2 x 150 ml), saturated $NaHCO_3$ (1 x 150 ml), and dried. Filtration and removal of solvent gave 0.11 g of a colorless oil which was void of olefinic pmr resonances. It appeared that the reagent brominated the olefinic bond bond.

Bromination with NBS A solution of 0.30 g (2.2 mmol) of 2-cyclooctene-1,4-dione (116), 0.77 g (4.3 mmol) of NBS, and 40 mg of benzoyl peroxide in 5 ml of CCl_4 was stirred at reflux under N_2 for 4 hr. The solution was cooled in an ice bath and filtered. Removal of solvent gave a near-quantitative recovery of starting material.

Attempts to initiate the reaction by irradiation with a 150 W tungsten lamp were unsuccessful. Quantitative recovery of starting material was also observed when a refluxing solution of ene-dione 116 and NBS in CCl_4 was irradiated for 6.25 hr.

The attempted addition of singlet oxygen to 1,6-dibromo-2,4-cyclooctadiene (102)

A solution of 2.66 g (10 mmol) of 102 and 30 mg of hematoporphyrin in 1000 ml of reagent grade acetone was irradiated using the general procedure for singlet oxygen addition. No uptake of oxygen occurred after 5 days of irradiation.

1,4-Dinitro-2,4,7-cyclooctatriene (121)

This compound was prepared in a manner similar to that described by Schechter and coworkers (118). Commercial dinitrogen tetroxide (N_2O_4, bp 10°C, Matheson) was purified by condensation at ice bath temperatures and passing oxygen through the liquid until the blue color disappeared. The liquid was then distilled into a septum-equipped bottle at -55° through a stainless transfer needle. The solid N_2O_4 was stored in a freezer (-21°C). Weighed amounts were most conveniently obtained by immersing the storage bottle in an ice bath to liquify the N_2O_4 and transferring the liquid *via* a precooled syringe into a tared volume of ice bath-cooled ether.

To a magnetically stirred solution of 3.12 g (30 mmol) of distilled cyclooctatetraene in 5 ml of ether (distilled from $LiAlH_4$) under N_2 in a previously flame dried 200 ml 3-neck inverse addition flask (equipped with an addition funnel and a glass wool plug for filtrations) was added over 45 min 2.7 g (30 mmol) of N_2O_4 in 60 ml of anhydrous ether. The solution was then stirred at -20° as the solution turned from green to yellow. The solvent was then removed by opening the stopcock to affect a filtration through the plug of glass wool. The orange solid was washed in the reaction flask with 10 ml of ether which was again removed via filtration. The orange solid (121) was not isolated, but used directly in the next step.

Disodium 2,5,7-cyclooctatriene-1,4-dinitronate (122)

This compound was prepared in a manner similar to that described in the literature (99). The crude 1,4-dinitro-2,5,7-cyclooctatriene (121) prepared above was suspended in 15 ml of ether and cooled to -20°. 1.92 g (36 mmol) of NaOMe in 10 ml of MeOH was added over 10 min via syringe. An orange solid precipitated immediately upon addition of the NaOMe. The solvent was removed through the glass wool plug, the solid was washed with ether (2 x 10 ml), and the orange solid was dried in vacuo. The powdery dark yellow solid thus isolated 2.4 g contained a small amount of NaOMe (10% by pmr). The net yield of 122 was 2.2 g (9.2 mmol, 31% from COT). The air stable solid (mp >250° (dec)) was soluble in H_2O, MeOH, and EtOH, but not in $CHCl_3$. The nitronate function was verified by a positive ferrous sulfate test (119). The spectral data were consistent with 122: pmr (D_2O) δ 6.02 (m, 4H), and 6.47 (s, 2H); ir (KBr) 1634 ($>=\overset{+}{N}$), 1467 ($-N<^{O}_{O}$), 1379, 1202, 1143, and 1061 cm^{-1}).

Reaction of disodium 2,5,7-cyclooctatriene-1,4-dinitronate (122) with $TiCl_3$

A solution of 0.300 g (1.25 mmol) of 122 in 15 ml of 1:2 H_2O-MeOH was added all at once to a solution containing 6.24 ml of 20% $TiCl_3$(aq) and 4.6 g of NH_4OAc in 15 ml of H_2O (pH ~6) under N_2 at room temperature. After 45 min the initially black-brown suspension had turned a dirty yellow. The reaction mixture was diluted with 50 ml of water and the aqueous solution was extracted with ethyl acetate (3 x 50 ml). The combined extracts were washed with water (2 x 50 ml), saturated $NaHCO_3$ (2 x 50 ml), saturated NaCl (1 x 50 ml), and dried. Filtration and removal of solvent gave 72 mg of a brown film. The pmr spectrum did not show any resonances characteristic of diene-dione 84 or triene-dione 85.

Reaction of disodium 2,5,7-cyclooctatriene-1,4-dinitronate (122) with HCl (Nef reaction)

The procedure used for this reaction was similar to that described by Wildman and Saunders (101). Twenty milliliters of a 1:1 H_2O-EtOH solution of 0.62 g (2.8 mmol) of dinitronate

122 was added over 45 min to a 0° solution of 22% HCl. Vigorous gas evolution was evident as each drop hit. The solution was then stirred 1.5 hr at 0°. The resulting brown, flocculent suspension was extracted with ether (4 x 50 ml). The combined ether extracts were washed with water (3 x 50 ml), saturated $NaHCO_2$ (1 x 50 ml), saturated NaCl (1 x 50 ml), and dried. Filtration and removal of solvent gave 0.26 g of an orange film which displayed a carbonyl absorption (1734 cm^{-1}) in the infrared spectrum, but the pmr and mass spectra did not show any peaks characteristic of the desired product 85.

Preparation of 1,4-dimethoxycyclooctatetraene (124) and 6-methoxy-2,4,6-cyclooctatriene-1-one (125)

1,4-Dibromocyclooctatetraene (2.62 g, 10 mmol), prepared by the method of Konz and coworkers (115), in 7 ml of DMSO (distilled from CaH_2) was added to a stirred solution of 2.70 g (50 mmol) of NaOMe in 20 ml of DMSO at 20°. The solution was stirred under N_2 for 15 hr at 20°. The reaction mixture was poured into 350 ml of ice water and the aqueous solution was saturated with NaCl and extracted with ether (3 x 150 ml). The combined ether extracts were washed with water (3 x 100 ml), saturated NaCl (1 x 100 ml), and dried. Filtration and removal of solvent gave 1.6 g of a red oil. The pmr of this oil showed it to be primarily 1,4-dimethoxycyclooctatetraene (124).

The crude product was placed on a column of neutral alumina (30 g, Act. I). Elution with hexane gave 0.95 g (5.8 mmol, 58%) of 124 as a yellow oil: pmr ($CDCl_3$) δ 3.46 (s, 6H), 4.79 (m, 2H), and 5.62 (m, 4H); ir (film) 1641 (C=C), 1202 (vinyl ether), 1164 and 1016 (vinyl ether) cm^{-1}; mass spectrum (70 eV) m/e (relative intensity) M^+ = 164 (64), 149 (100), 133 (26), 91 (25), and 78 (21).

Elution with ether-hexane (30:70) afforded 125 as a golden oil: pmr ($CDCl_3$) δ 2.96 (d, 2H, J = 8 Hz), 2.98 (d, 2H, J = 8 Hz), 3.61 (s, 3H), 3.68 (s, 3H), and 5.46-6.84 (m, 10H); ir ($CHCl_3$) 1646 (C=O), 1621 (C=C), and 1154 cm^{-1}; mass spectrum (70 eV) m/e (relative intensity) M^+ = 150 (100), 135 (26), 122 (85), and 107 (90).

Hydrolysis of 1,4-dimethoxycyclooctatetraene (124)

1,4-Dimethoxycyclooctatetraene (124) 0.33 g (2.0 mmol) and 20 mgm of p-toluene sulfonic acid in 10 ml of 95% EtOH were stirred at reflux under N_2 for 6 hr. The solution was cooled and diluted with 25 ml of water. The aqueous solution was extracted with ethyl acetate (2 x 30 ml). The combined extracts were washed with saturated $NaHCO_3$ (2 x 50 ml), saturated NaCl, and dried. Filtration and removal of solvent gave a dark orange oil. A pmr spectrum of this material indicated that starting material had been consumed, and that the crude product was primarily a mixture of isomers 125 and 126. No pmr resonances of dione 84 were seen.

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