Aliphatic Semidiones. XXVII. Radical Anions Derived from Bicyclo[4.*n*.0]alk-3-ene-2,5-diones[1]

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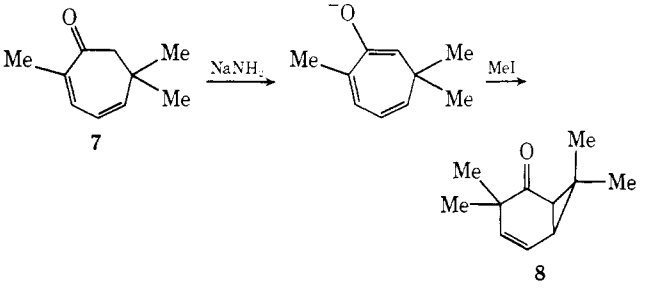
Abstract: Hyperfine splitting constants have been assigned to the 2,5-semidiones (radical anions of Δ^3-2,5-diones) in the bicyclo[4.1.0]heptane, bicyclo[4.2.0]octane, and bicyclo[4.2.0]oct-7-ene series and to the *p*-benzosemiquinones derived from benzocyclobutenes. INDO and EH-SCF calculations for the parent semidiones are reported as a function of geometry. Evidence for a dynamic valence isomerization involving a 95:5 ratio of *anti*-7-methyl- and *syn*-7-methylbicyclo[4.1.0]heptane-2,5-semidione and an undetected monocyclic cycloheptatriene derivative is presented. Bicyclo[4.2.0]oct-7-ene-2,5-semidiones gave no evidence of isomerizing to the monocyclic cyclooctatraene derivatives. Treatment of bicyclo[4.2.0]octane- or bicyclo[4.2.0]oct-7-ene-2,5-semidiones with excess oxygen formed *p*-semiquinones of benzocyclobutene.

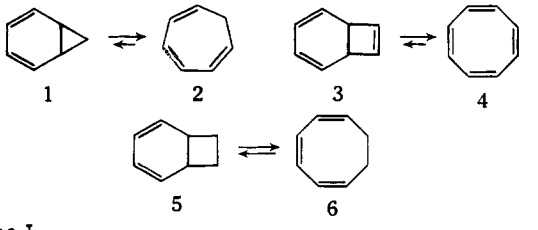
Valence isomerization may potentially occur in numerous unsaturated molecules, including the well-known examples illustrated in Chart I. In the case of the norcaradiene (**1**)-cycloheptatriene (**2**) system, the equilibrium lies far to the right since norcardiene cannot be detected in cycloheptatriene (tropilidene) by spectral methods.[4] Similarly the equilibrium for the bicyclo[4.2.0]octa-2,4,7-triene (**3**)-cyclooctatetraene (**4**) system lies far to the right as shown in Chart I; in this case, however, the isomerization of **3** to **4** is quenched at −78° and **3** is stable if prepared and stored at low temperatures.[5] The bicyclo[4.2.0]octa-2,4-diene (**5**)-1,3,5-cyclooctatriene (**6**) valence isomerization proceeds only at temperatures above 80°, and thus both pure **5** and **6** can be separately isolated at room temperature.[6]

Valence isomerization is also known to occur in some enolate anions. Treatment of eucarvone (**7**), for example, with sodium amide followed by the addition of methyl iodide affords the bicyclic ketone **8**.[7]



7 **8**

Chart I



1 **2** **3** **4** **5** **6**

Scheme I

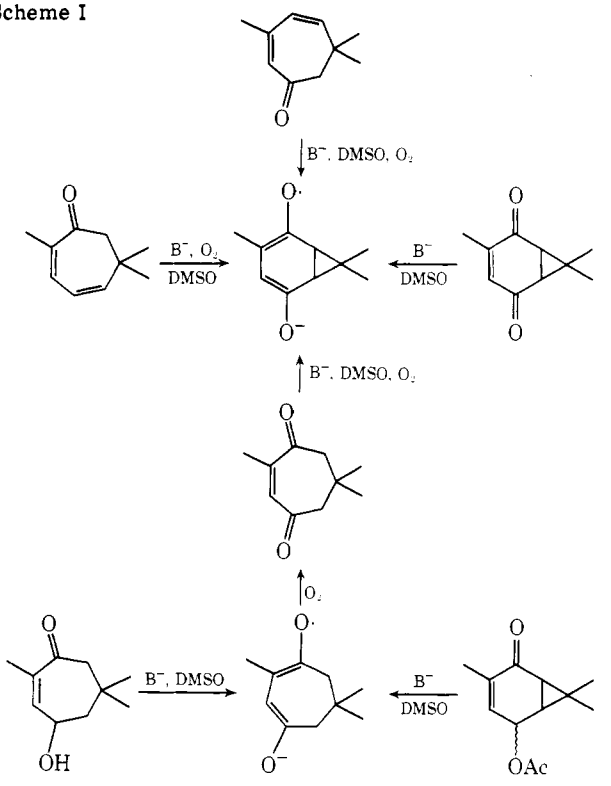
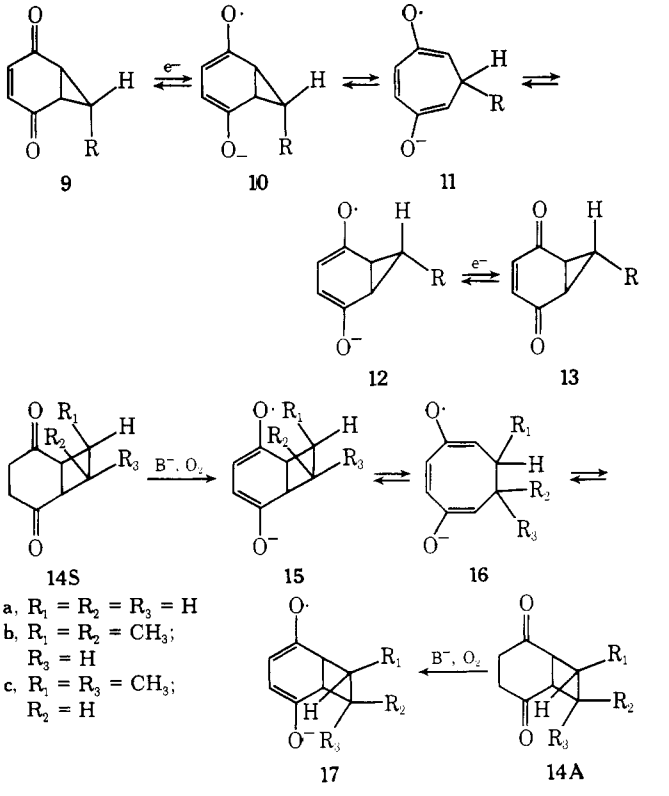


Chart II



9 **10** **11** **12** **13**

14S **15** **16**

a, $R_1 = R_2 = R_3 = H$
b, $R_1 = R_2 = CH_3$; $R_3 = H$
c, $R_1 = R_3 = CH_3$; $R_2 = H$

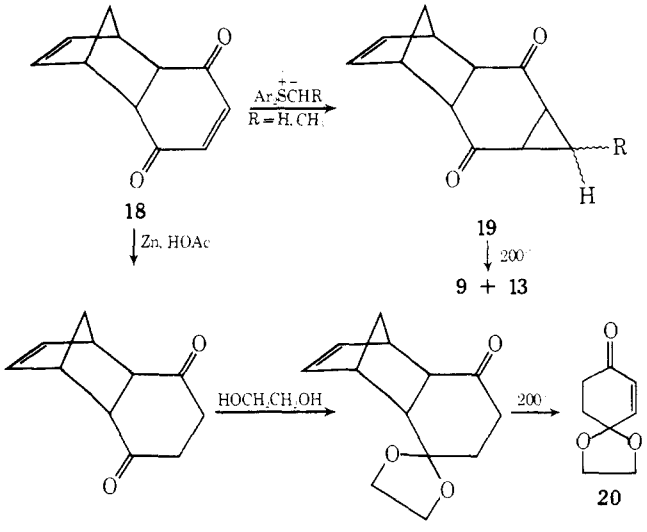
17 **14A**

We have demonstrated the occurrence of valence isomerization in the processes summarized in Scheme I.[8,9] The spontaneous formation of semidiones from hydroxy ketones in basic solution is well known[10] as well as the ability of basic DMSO solutions to reduce by one electron a variety of unsaturated ketones.[11] From the results summarized in Scheme I, it is not possible to state at what oxidation stage (enolate anion, radical anion, dienolate dianion) valence isomerization occurred. The present work was initiated in hopes of obtaining evidence for valence isomerization at the radical anion stage for 1,4-semidiones related to the norcaradiene-cycloheptatriene system as well as the cyclooctatriene-bicyclo[4.2.0]octa-2,4-diene analogs (Chart II).

Results and Discussion

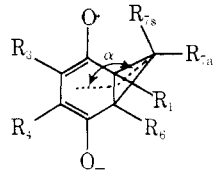
Synthesis. Diones of structure **9** and **13** were synthesized by addition of diphenylsulfonium ylides to the benzoquinone-cyclopentadiene Diels–Alder adduct[12] followed by pyrolysis (Scheme II). The semidiones were synthesized either by electrolytic reduction of the diones or by reduction with base in DMSO.[11] Semidiones **15** and **17** were synthesized from the saturated 1,4-diones by oxidation in basic solution, a process for which there are numerous other examples.[9,13] Diones **14a–c** were synthesized according to Scheme III from the monoethylene ketal of cyclohex-2-ene-1,4-dione (**20**).[14]

Scheme II



Esr Spectra of Bicyclo[4.1.0]hepta-2,5-semidiones. Figure 1 gives the esr spectra of bicyclo[4.1.0]hepta-2,5-semidione and its *syn*- and *anti*-7-methyl derivatives generated at 25° by *in situ* electrolytic reduction in DMF of the bicyclo[4.1.0]hept-3-ene-2,5-diones. The assignment of hyperfine splitting constants (hfsc) for these semidiones and others previously reported[8] gives a consistent picture (Chart III).

Chart III



27a R_1–R_7 = H; a^H = 5.48 (H-3,4), 3.01 (H-1,6), 1.65 (H-7a), 0.75 (H-7s) G
b R_1–R_6 = H, R_{7a} = H, R_{7s} = CH_3; a^H = 5.50 (H-3,4), 3.12 (H-1,6), 1.45 (H-7a) G
c R_1–R_6 = H, R_{7s} = H, R_{7a} = CH_3; a^H = 5.54 (H-3,4), 3.01 (H-1,6), 0.88 (H-7s), 0.88 (CH_3) G
d R_1–R_6 = CH_3, R_7 = H; a^H = 5.20 (CH_3, C-3,4), 0.25 (CH_3, C-1,6), 1.95 (H-7a), 0.87 (H-7s) G
e R_1,R_3 = *t*-Bu, R_4–R_7 = H; a^H = 4.90 (H-4), 2.40 (H-6), 1.40 (H-7a), 0.90 (H-7s), 0.20 (6 or 9 hydrogens) G
f R_1,R_4,R_6 = H, R_3,R_7 = CH_3; a^H = 4.95 (CH_3, C-3), 4.68 (H-4), 3.45, 3.15 (H-1,6), 0.82 (CH_3-7a) G
g R_1 = D, R_4,R_6 = H, R_3,R_7 = CH_3; a^D = 0.52 (D-1); a^H = 4.95 (CH_3, C-3), 4.68 (H-4), 3.15 (H-6), 0.82 (CH_3-7a) G
h R_1,R_6 = D, R_2 = R_3 = R_{7s} = H, R_{7a} = CH_3; a^D = 0.48 (D-1,6); a^H = 5.54 (H-3,4), 0.88 (H-7s; CH_3, *anti*-C-7) G
i R_1–R_6 = H, R_7 = CH_3; a^H = 5.4 (H-3,4), 3.2 (H-1,6), 0.83 (CH_3, *anti*-C-7) G
j R_3–R_4 = benzo, R_1,R_6,R_7 = H; a^H = 3.20 (H-1,6), 1.64 (H-7a), 0.86 (H-7s), 1.28 (H-*o*), 0.10 (H-*m*) G

The hfsc's in this system have sufficient constancy so that tricyclic structures can be excluded and bicyclic structures (**28B, 29B**) can be assigned to the semidiones formed by re-

Scheme III

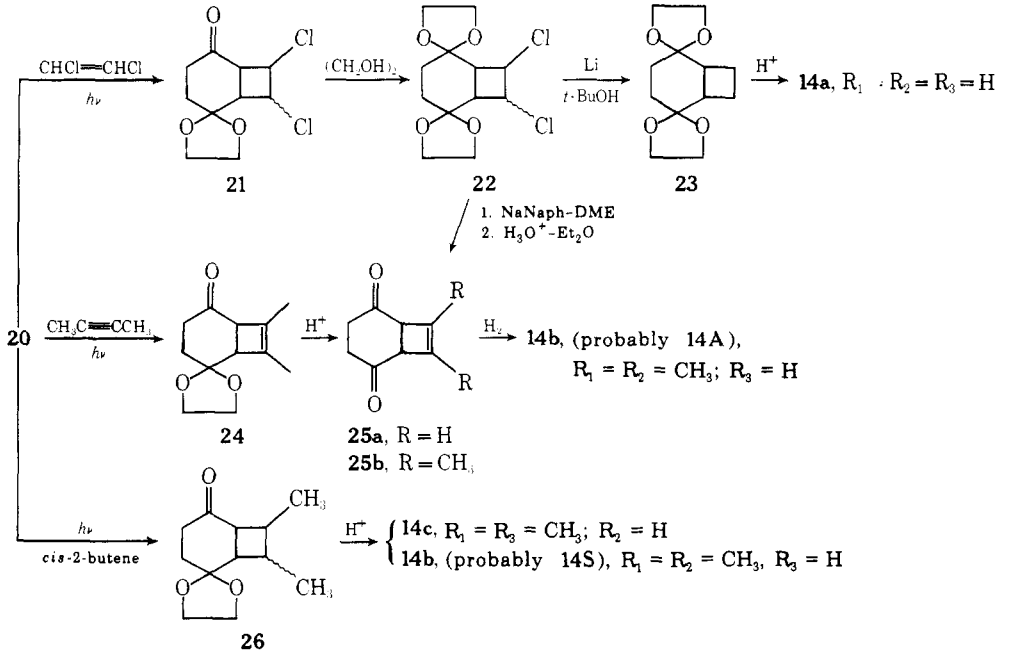


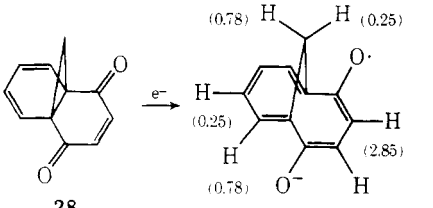
Table I. Hyperfine Splitting Constants Calculated for **27a**[a]

Position	α 106° EH	α 106° INDO	α 110° EH	α 110° INDO	α 118° EH	α 118° INDO	Exptl
1,6	1.77	0.18	2.21	0.10	2.85	0.77	3.00
3,4	−4.80[b]	−3.54	−4.74[b]	−3.49	−4.89[b]	−3.71	5.48
7a	0	−0.78	0	−0.79	0	−0.47	1.65
7s	0	−0.78	0	−1.65	0	−1.18	0.75

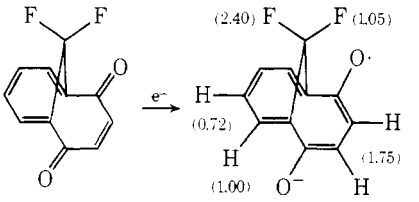
[a] d(C-2-C-3) = d(C-4-C-5) = 1.42, d(C-3-C-4) = 1.38 Å, all other d(C–C) = 1.54, d(C–H) = 1.09, and d(C–O) = 1.22 Å, all hydrogen atoms are positioned so that all H-C-C angles are equal for a given carbon atom. [b] $a^H = -24\rho_{C3,4}^{\pi}$.

duction of diones **28** and **29** by propiophenone enolate anion in DMSO at 25° (Scheme IV).[8,15]

Scheme IV



28 **28B** (a^H in G)



29 **29B** (a^H, a^F in G)

Eucarvone or the isomeric 1,1,4-trimethylcyclohepta-2,4-dien-6-one both yielded upon oxidation the bicyclic semidione **27f** (Scheme I) which was also observed as the reduction product of Δ^3-2,5-carenedione in basic DMSO or from oxidation of either Δ^3-2-hydroxycaren-5-one or 2,6,6-trimethylcyclohept-2-ene-1,4-dione in basic DMSO. Oxidation of 6,6-dimethylcyclohept-2-ene-1,4-dione in basic DMSO-d_6 gave the bicyclic semidione **27i.** When prepared by reduction of Δ^3-2,5-carenedione or by the immediate oxidation of eucarvone in basic DMSO-d_6, no deuterium incorporation was observed in **27f.** However, when the eucarvone was allowed to undergo hydrogen-deuterium exchange before oxidation, the monodeuterated semidione **27g** was observed. The *syn*-7-methylbicyclo[4.1.0]hept-3-ene-2,5-dione in basic DMSO-d_6 gave immediately **27h** in which both bridgehead hydrogens had been exchanged while conditions which yield the monocyclic 2,6,6-trimethylcycloheptane-1,4-semidione (Scheme I) have been observed in DMSO-d_6 to yield the 3,5,5,7,7-pentadeuterio derivative.[9]

The esr hfsc's observed for semidiones derived from bicyclo[4.1.0]hept-3-ene-2,5-dione seem reasonable in terms of MO calculations. The but-2-ene-1,4-dione radical anion has a calculated spin density at (C-2,3) of 0.2018 (Hückel), 0.2085 (McLachlan).[16] Using the standard value of Q_{CH}^H = −24 G leads to predicted values of $a_{3,4}{}^H$ of 4.84–5.00 G (observed, 4.7–5.9 G) for **27.** Extended Hückel SCF calculations[17] gave good agreement with a^H for H-1,3,4,6 for **27a** (Table I) but predict no hfs for H_{7a} or H_{7s}.[18] INDO calculations[19] with the same geometry gave good agreement with the experimental values of a^H for H-3,4,7a and 7s but rather poor agreement for H-1,6 (Table I).

The signs of $a_7{}^H$ calculated by the INDO approximation are in agreement with out previous analysis of this interaction.[8] Since the methylene group is in a nodal plane of the π-system, spin delocalization with electron transfer cannot be involved[18] and introduction of the electron spin into the

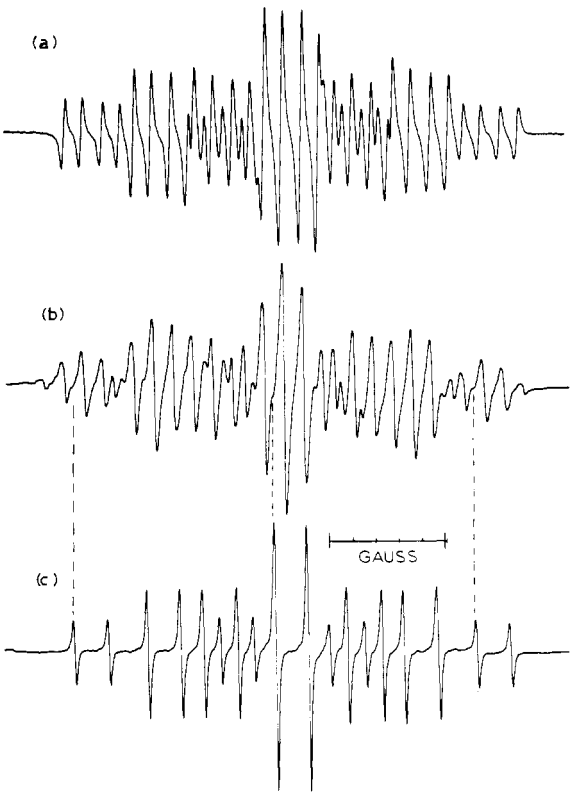
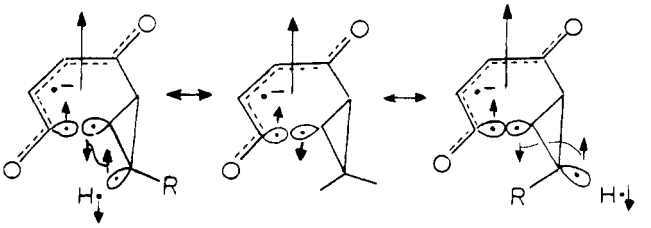


Figure 1. First derivative esr spectra of bicyclo[4.1.0]hepta-2,5-semidiones: (a) the unsubstituted system (**27a**), (b) *anti*-7-methyl substituent (**27c**), (c) *syn*-7-methyl substituent (**27b**). Mixtures of (b) and (c) contain resolved lines for (c) at only the three positions indicated by dotted vertical lines.

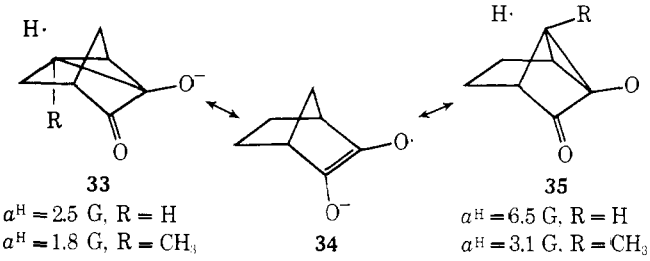
σ-framework by spin polarization without electron transfer is required (**31**).[8]



31 **30** **32**

a^H = 0.75 G, R = H; a^H = 0.88 G, R = CH_3 — a^H = 1.65 G, R = H; a^H = 1.45 G, R = CH_3

This should be contrasted to systems such as bicyclo[2.2.1]heptanesemidione (**34**) where the methylene groups at C-7 (or C-5,6) are not in a node of the spin label and electron transfer by delocalization (homohyperconjugation) occurs to the anti hydrogen at C-7 (**35**) or the exo hydrogen atoms at C-5,6 (**33**).[20,21] As shown in the structures this spin transfer mechanism is impeded by methyl substitution at the backside of the carbon-hydrogen bond involved (syn at C-7, endo at C-5,6). Structures **31** and **32** do not involve



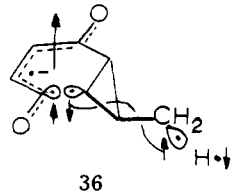
33 34 35

$a^H = 2.5$ G, R = H; $a^H = 1.8$ G, R = CH_3

$a^H = 6.5$ G, R = H; $a^H = 3.1$ G, R = CH_3

backside bonding. Thus, methyl substitution at the syn C-7 position does not affect the spin polarization–hyperconjugation interaction in **32.** When the geometry and nodal properties allow both mechanisms to compete it should be observed that methyl substitution in the syn (C-7) position will make a_{anti}^H less positive and will result in a decrease in magnitude of a^H when a^H is positive (homohyperconjugation predominant) but an increase in magnitude of a^H when a^H is negative (spin polarization predominant).

Although the stereoselectivity of the interaction (hyperconjugation) is low for the hydrogen atoms in the 7-position in **27,** the interaction is quite stereoselective for methyl groups at C-7. The *anti*-7-methyl group interacts much more strongly than the *syn*-7-methyl group. Once the spin is introduced into the σ system by spin polarization (**30**) a favorable transoid coplanar (W-plan) arrangement of bonds exists between the spin polarized carbon orbital and the *anti*-7-methyl substituent (**36**) allowing a backside homoconjugative interaction[21] to occur.

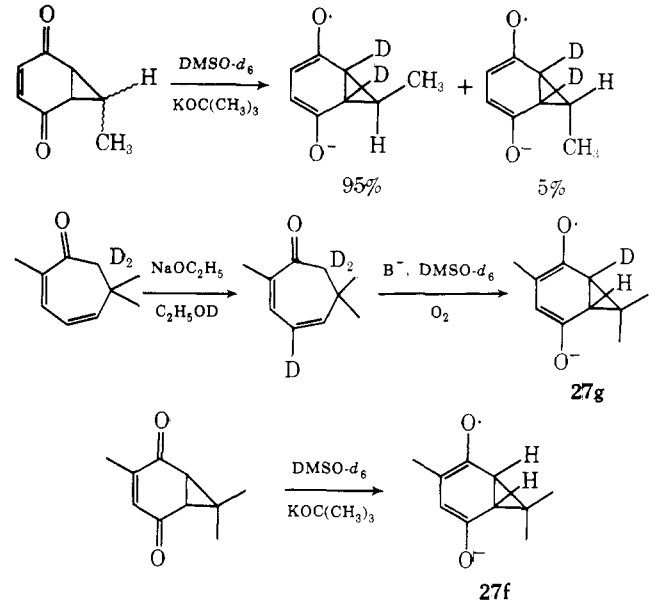


36

The observed hfsc for the syn and anti hydrogen atoms at C-7 and for the *anti*-7-methyl group in **27** can serve as a model for dissecting hfsc in systems where both spin polarization and spin delocalization can occur. The relative magnitudes of the interactions in this system where spin delocalization is not involved are *syn*-7-H (~1), *anti*-7-H (~2), *syn*-7-CH_3 (~0), and *anti*-7-CH_3 (~1).

Valence Isomerization in Bicyclo[4.1.0]hepta-2,5-semidiones. The independent existence of *syn*- and *anti*-7-methyl derivatives (**27b,c**) would appear to exclude the valence isomerizations **10** ⇄ **11** ⇄ **12** (R = CH_3) from further consideration. However, when either **9** or **13** was treated with potassium *tert*-butoxide in DMSO the same mixture of ~5% of **10** (=**27b**) and ~95% of **12** (=**27c**) was immediately observed. This observation requires that either the radical ions or the dianions ($\mathbf{9}^{2-}$, $\mathbf{13}^{2-}$) or the enolate dianions have interconverted. Evidence for ionization of bridgehead protons to give enolate anions was furnished by the observation that in DMSO-d_6 **13** (R = CH_3) gave semidione **27h** with deuterium atoms at C-1,6 (the expected ~5% of the *syn*-7-methyl iosmer could not be detected because of the complexity of the esr spectrum of **27h**). This result is somewhat surprising because when 4,7,7-trideuterioeucarvone was oxidized in basic DMSO-d_6 only a monodeuterio semidione (**27g**) was detected while from Δ^3-carene-2,5-dione the undeuterated semidione was observed (Scheme V). It appears that the *exo*-7-methyl substituent in **27f** or **27g** hinders hydrogen–deuterium exchange at C-1 and C-6, presumably by a steric effect. Other examples of steric hindrance to ionization by substituents have been reported for bicyclic semidiones in the [3.1.0]hexane system.[18]

Scheme V



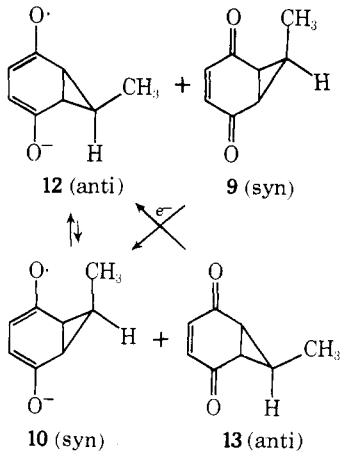
95% 5%

27g

27f

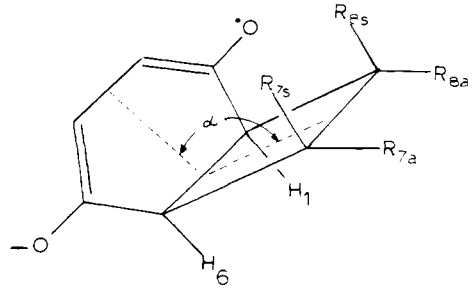
Direct evidence for the interconversion of **10** or **12** to **11** is not provided by either the electrolytic reduction or the chemical reduction by base in DMSO. However, a slow interconversion of **10** ⇄ **11** ⇄ **12** is not excluded by either of these results because an analysis of the system cannot be made without also considering the equilibria **9** ⇄ **10** and **12** ⇄ **13** (or the equivalent **10** + **13** ⇄ **12** + **9**). In fact, when a mixture of 90% **13** (*anti*-methyl) and 10% of **9** (*syn*-methyl) was reduced electrolytically in DMF in the absence of base, an intense esr signal of *only* the *syn*-semidione (**10**) was detected during the electrolysis. Thus the *syn*-7-methyl dione (**9**) is much more easily reduced than the *anti*-7-methyl dione (**10**). We thus turned our attention to the effect of time and the extent of reduction on the esr signals observed from **9** and **13.** The *anti*-7-methyl dione in DMF gave during electrolysis a strong esr signal of the *anti*-semidione free of the syn isomer. Upon cessation of electrolysis the strength of the esr signal decreased and the esr spectrum of the *syn*-semidione appeared so that after 15 min the ratio of anti:syn semidiones was *ca.* 96:4. When the *syn*-dione was reduced electrolytically (to a small extent) and the reduction halted, no trace of the anti isomer could be found over the period of 1 hr that the esr spectrum could be detected. When the *syn*-dione was completely or nearly completely reduced electrolytically over a period of 30 min, the final esr spectrum was clearly that of the *anti*-semidione with a few per cent of the cis isomer. These results are all nicely correlated if the valence isomerization **10** ⇄ **11** ⇄ **12** is allowed together with rapid electron transfer between diones and semidiones. In the presence of excess *syn*-7-methydione any of the *anti*-7-methylsemidione formed by valence isomerization would yield by electron transfer the *syn*-7-methylsemidione (Scheme VI). Thus, the *anti*-7-methylsemidione can be observed only when the concentration of the *syn*-7-methyldione is very low. The reactions of Scheme VI provide a mechanism for the isomerization of **9** to **13** once some of the semidione has been formed. However, the rate of **10** ⇄ **12** appears to be slow as evidenced by the observation that when **12** is being formed rapidly by electrolysis of **13, 10** cannot be detected and can be seen only after the electrolytic reduction has been halted. Since semidiones are in equilibrium with diones and their dianions, it is also possible that the syn–anti interconversion may involve the latter species, *i.e.*, $\mathbf{10}^{2-}$ ⇄ $\mathbf{12}^{2-}$.

Scheme VI



Esr Spectra of Bicyclo[4.2.0]octa-2,5-semidiones. Figure 2 gives the esr spectra of bicyclo[4.2.0]octa-2,5-semidione (**37a**) and the syn,anti-7,8-dimethyl (**37b**) derivative in DMSO solution. The semidiones were prepared by oxidation of the saturated 1,4-diones in basic DMSO solution or DMSO-d_6 (**37c**). The assignment of the hfsc gives a consistent picture (Chart IV) for a cis ring fusion in the bicyclic semidione.

Chart IV



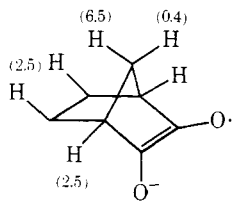
37a, $R_7 = R_8 = H$; a^H = 5.85 (H-3,4), 3.48 (H-1,6), 0.32 (2), 0.18 (2) G

b, $R_{7s} = R_{8a} = H$, $R_{7a} = R_{8s} = CH_3$; a^H = 5.85 (H-3,4), 4.60 (H-1 or H-6), 2.60 (H-6 or H-1), 0.39 (1), 0.25 (1) G

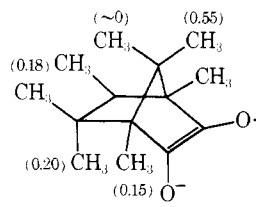
c, H-1,3,4,6 = D, $R_{7s} = R_{8a} = H$, $R_{7a} = R_{8s} = CH_3$; a^D = 0.87 (D-3,4), 0.69 (D-1 or D-6), 0.39 (D-6 or D-1); a^H = 0.39 (1) 0.25 (1) G

d, *cis*-7,8-dimethyl; a^H = 5.90 (H-3,4), 3.75 (H-1,6), 0.32 (2) G

The hfs of hydrogen atoms in the ethano bridge of **37a** are difficult to assign without a knowledge of the sign of a^H. INDO calculations (Table II) indicate that $a_{7a,8a}{}^H$ is positive and greater than $a_{7s,8s}{}^H$. The absence of hfs by the anti methyl group in **37b** suggests that spin polarization and delocalization mechanisms at this position cancel each other as is the case for the *anti*-7-methyl group in 1,7,7-trimethylbicyclo[2.2.1]heptane-2,3-semidione (**38b**).[21]



38a
(a^H in G)



38b
(a^H in G) composite spectra of several methyl derivatives of **38a**

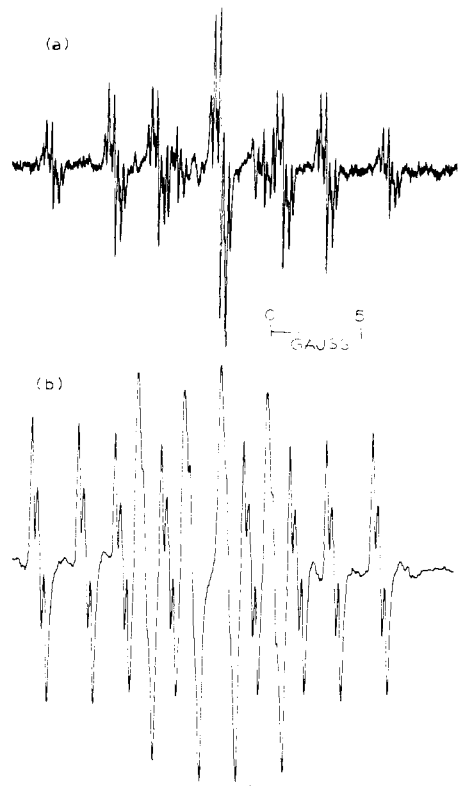


Figure 2. First derivative esr spectra of (a) bicyclo[4.2.0]octa-2,5-semidione and (b) *syn,anti*-7,8-dimethylbicyclo[4.2.0]octa-2,5-semidione in DMSO solution at 25°.

The hfs pattern observed for **37b** completely excludes a trans ring fusion. The nonequivalence of bridgehead hydrogen atoms in **37b** (a^H = 4.60, 2.60 G) indicates that the C(2)-C(1)-C(8) bond angle is larger than the C(5)-C(6)-C(7) angle (the syn methyl is at C-8), an arrangement which allows the syn methyl group to move away from the six-membered ring to relieve steric interactions and which makes the C(1)-H bond more parallel to the carbon p_z-orbital at C-2; *i.e.*, $a_1{}^H$ = 4.6 G.

Two isomeric *cis*-7,8-dimethylbicyclo[4.2.0]octane-2,5-diones (**14b**) were prepared (Scheme III). In view of the spectrum observed for **37b,** we expected a considerable difference between the esr spectra of the *syn,syn-* and *anti,anti*-dimethylsemidiones. Dione **14b** prepared by catalytic hydrogenation gave a single paramagnetic species (**37d**) upon oxygenation in basic DMSO (Figure 3a). The values of a^H = 5.90 (2), 3.75 (2), and 0.32 (2) G are quite similar to the hfs reported for **37a,** and it appears that the geometry at C-1 and C-6 is quite similar for **37a** and **37d.** The other cis dione (from the photochemical addition of 2-butene, Scheme III) gave a mixture of radical anions when oxidized in basic solution. With time and further oxygenation the spectrum of Figure 3b resulted. In Figure 3b four lines due

Table II. INDO Calculated Hyperfine Splitting Constants (G) for **37a**[a]

Position	α 105°	α 111°	α 120°	Exptl
H-3,4	−4.29	−4.14	−4.50	5.85
H-1,6	−0.30	−0.45	−0.78	3.48
H-7a,8a	+0.80	+0.56	+0.38	0.32
H-7s,8s	−0.16	−0.03	+0.07	0.18

[a] d(C-2-C-3) = d(C-4-C-5) = 1.42, d(C-3-C-4) = 1.37 Å, all other d(C-C) = 1.54, d(C-H) = 1.09, and d(C-O) = 1.22 Å. All hydrogen atoms are positioned so that all H-C-C angles were equal for a given carbon atom.

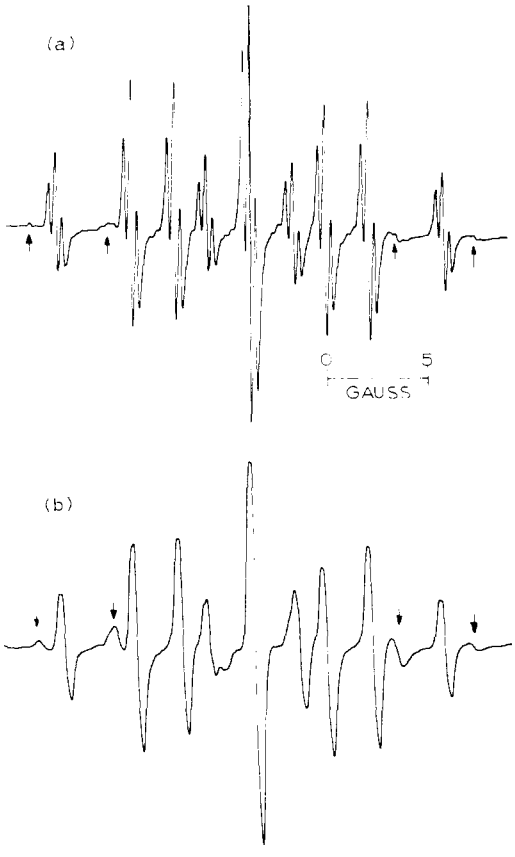


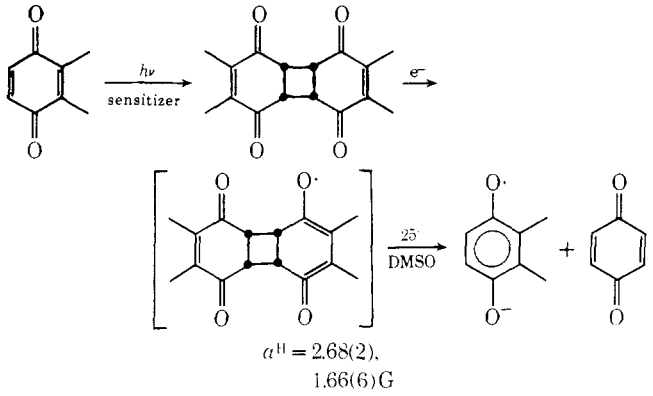
Figure 3. First derivative esr spectra of *cis*-7,8-dimethylbicyclo[4.-2.0]octa-2,5-semidione prepared by oxidizing the 1,4-diones in basic DMSO solution: (a) dione prepared from **25b**, (b) dione prepared from **26**.

to another radical anion are indicated by arrows, and it is seen that traces of this species are also present in spectrum 3a. Figures 3a and 3b are very similar except that the 0.32 G triplet is not resolved in 3b. We conclude that there has been an isomerization of one of the systems at either the dione, semidione, or dianion stage. In basic solution enolization of the bridgehead hydrogen atoms occurs as evidenced by the formation of the tetradeuterio derivative **37c** in the trans dimethyl system in DMSO-d_6. Thus isomerization of one cis dimethyl species to the other could involve stepwise epimerization of the bridgehead positions with the intermediacy of a trans fused ring junction. It would seem that the most logical structure for **37d** would be the anti,anti dimethyl structure (**37**, $R_{7s} = R_{8s} = H$, $R_{7a} = R_{8a} = CH_3$). If this is correct then in **37a** the syn hydrogens at C-7,8 must have the larger hfsc (0.32 G) and the anti the lowest hfsc (0.18 G). The possibility exists that there is a change in sign with the syn hydrogen having a negative a^H (from spin polarization) while the anti hydrogens have a more positive (either negative or positive in sign) value of a^H resulting from the net effect of spin polarization and delocalization.

Quinone photodimers (Scheme VII) appeared to present interesting percursors to bicyclo[4.2.0]octane-2,5-semidiones. However, upon electrolytic reduction of the photodimer of 2,3-dimethylbenzoquinone[22] in DMF, a mixture of radical anions was formed in which 2,3-dimethyl-*p*-benzosemiquinone could be identified. Apparently this is another example[9] wherein by addition of an electron to the LUMO a 2 + 2 cycloaddition becomes thermally reversible.

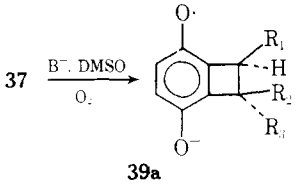
***p*-Benzocyclobutene Semiquinones.** Treatment of **37** with additional small amounts of oxygen produced **39** (Chart V).[23] The parent system **39a** had a half-life of ~5 min (from esr) whereas **39b** and **39c** had $t_{1/2} \sim 70$ min. The

Scheme VII



corresponding semiquinones of benzocyclopropene and benzocyclobutadiene were not detected upon overoxidation of **27** or **40a** but direct evidence for benzocyclobutadiene formation will be presented.

Chart V



39a

39a, R_1–R_3 = H; a^H = 2.46 (2), 1.93 (4) G
b. $R_1 = R_2 = CH_3$, R_3 = H; a^H = 2.51 (2), 1.77 (2) G
c. $R_1 = R_3 = CH_3$, R_2 = H; a^H = 2.51 (2), 1.70 (2)G

The small value of $a_{CH_2}{}^H$ observed for **39a** is in agreement with the observations previously made for the related cyclobuta[*b*]naphthalene-3,8-semiquinone[24] (see Chart VI). The observed value of $a_{CH_2}{}^H = 2.94$ G in this semiquinone was considerably less than the value of 4.7 G predicted from the Hückel spin density at C-1 with a value of $Q = 51$ G.[24] The discrepancy was explained in terms of the influence of strain on the spin density distribution using Streitweiser's "hybridization effect model"[25] which makes the ring juncture carbon atoms of a strained ring less electronegative (a smaller Coulomb integral) and the carbon atom α more electronegative (a larger Coulomb integral). The same effect apparently applies to **39a** to the same degree since the ratios of $a_{CH_2}{}^H/a_{CH_3}{}^H$ for the 2,3-ethano- and 2,3-dimethyl-*p*-semiquinones are very similar in the benzene (1.95/1.71 = 1.14) and naphthalene (2.94/2.51 = 1.16) series.

An alternate and probably preferable explanation of the low values of $a_{CH_2}{}^H$ in **39a** and the naphthoquinone analog involves the increased importance of 1,3 overlap in the cyclobutane ring and the antisymmetric nature of the HOMO in these radical anions.[21,26]

Bicyclo[4.2.0]oct-7-ene-2,5-semidiones. Semidiones **40** and **41** constitute a pair of valence isomers (Chart VII). Oxidation of the 1,4-diones **25a,b** formed **40a,b** in DMSO and the tetradeuterio derivative of **40b** in DMSO-d_6 (a^D = 0.88 (2), 0.76 (2), a^H = 0.14 (6) G).

Electrolytic reductions or treatment with basic DMSO of substituted bicyclo[4.2.0]oct-3,7-diene-2,5-diones[29] yielded **40c** and **40d** with hfsc in agreement to the assignment for **40a,b** and with no indication of a reversal of the 2 + 2 photochemical cycloaddition reaction. In DMSO-d_6 **40c** slowly exchanged the hydrogen atom with 4.61 G to give a^D = 0.70 G.

Chart VI. a^H in G[27,28]

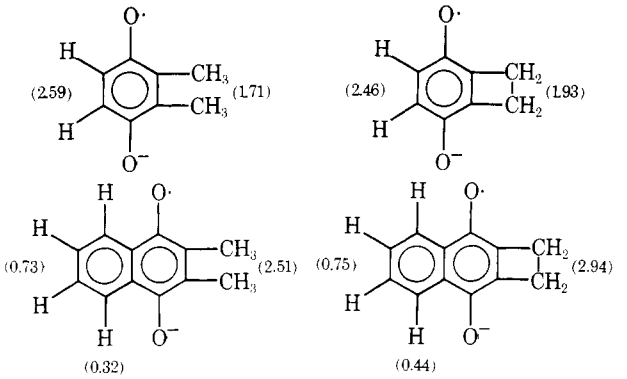
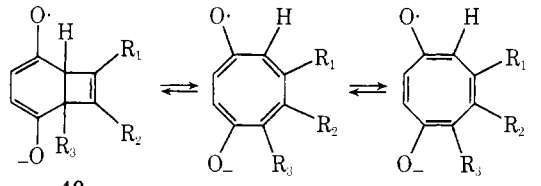


Chart VII

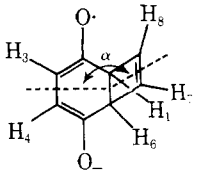


40 41

a, R_1-R_3 = H; a^H = 5.58 (2), 5.08 (2), 0.44 (2) G
b. $R_1 = R_2 = CH_3$, R_3 = H; a^H = 5.75 (2), 5.10 (2), 0.14 (6) G
c, R_1 = H, $R_2 = C_6H_5$, $R_3 = CH_3O$; a^H = 5.62, 5.13, 4.61, 0.22 G
d, $R_1 = CH_3$, $R_2 = C_6H_5$, $R_3 = CH_3O$;
a^H = 5.63, 5.10, 4.70, 0.49 (3) G

The magnitudes of $a_{CH}{}^H$ and $a_{CH_3}{}^H$ for $R_1 = R_2$ = H or CH_3 as well as the magnitude of $a_{CH}{}^H$ at the bridgehead positions supports the bicyclic structures **40.** Since the system has not yet been entered from a monocyclic precursor, it is impossible to state whether the isomerization of **41** to **40** will occur readily or if an equilibrium greatly favoring **40** over **41** exists.

In Table III are given the EH-SCF and INDO calculations for **40a.** The INDO calculation again gives a poor pre-



40a

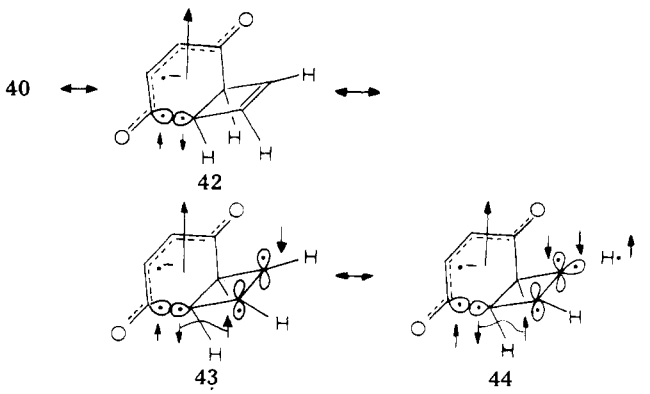
diction for the α (bridgehead) positions. Direct spin transfer from the 1,4-semidione spin label to the isolated double bond in **40a** would not be expected because the HOMO's have different symmetries.[21] Apparently either spin transfer by delocalization directly to hydrogen atoms H-7 and H-8 can occur (required by the EH treatment), or alternately, in the INDO treatment spin polarization without electron transfer can be involved, *e.g.,* structures **42–44,** wherein a negative electron spin density is introduced into the olefinic system by spin polarization (**42**) and conjugation (**43**). Although the symmetries of the HOMO's in the spin label and double bond are different, it is observed at C-7,8 that $a_{CH}{}^H$ (0.9 G for **40a,** 0.23 G for **40c**) $\approx a_{CCH_3}{}^H$ (0.14 G for **40b,** 0.43 G for **40d**) suggestive of unpaired spin density in the π-system since $-Q_{CH}{}^H \approx Q_{CCH_3}{}^H$. Such an effect is consistent with **40** ↔ **42.** Over-oxidation of **40a** or **40b** pro-

Table III. Hyperfine Splitting Constants Calculated by EH-SCF and INDO Methods for **40a**[a]

	α				
	115°		125°		
Position	EH	INDO	EH	INDO	Exptl
H-3, H-4	−5.22	−3.83	−5.38	−3.71	|5.58|
H-1, H-6	+7.76	+17.1	+7.04	+1.41	|5.08|
H-7, H-8	+0.69	+0.62	+0.78	+1.12	|0.44|

[a] d(C-2–C-3) = 1.42, d(C-3–C-4) = 1.37, d(C-7–C-8) = 1.38 Å, all other d(C–C) = 1.54, d(C–H) = 1.09, d(C–O) = 1.22 Å.

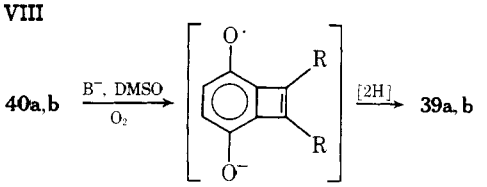
duced **39a** and **39b,** respectively. The cyclobutadiene intermediate **45** is implicated because the cis stereochemistry in



40 42 43 44

the resulting benzocyclobutene derivative **39b** suggests that perhaps two hydrogen atoms (Scheme VIII) are transferred to **44** by some concerted process.[30]

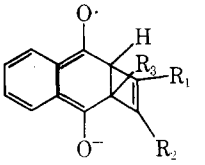
Scheme VIII



45

A similar phenomenon was encountered in an examination of the benzo derivatives of **40,** semidiones **46a–d** (Chart VIII).

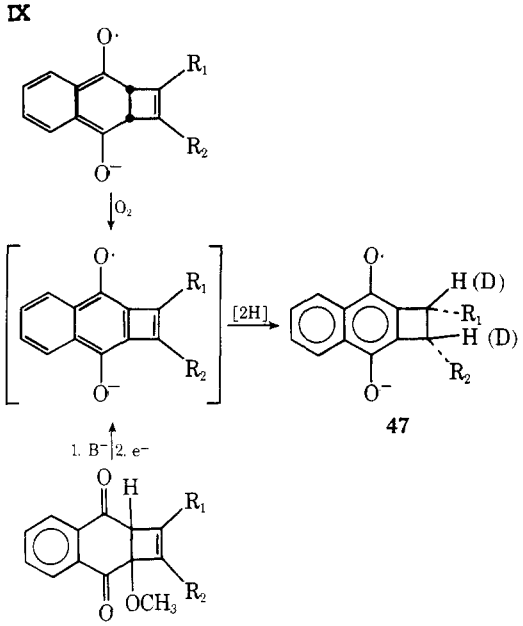
Chart VIII



46a, $R_1 = R_2 = CH_3$, R_3 = H;
a^H = 5.43 (2), 2.48 (2) 0.24 (2), 0.21 (6) G
b, $R_1 = R_2 = C_6H_5$, R_3 = H; a^H = 6.05 (2), 2.33 (2) G
c, $R_1 = R_2 = C_6H_5$, $R_3 = CH_3O$
d, R_1 = H, $R_2 = C_6H_5$, $R_3 = CH_3O$

Over-oxidation of **46a** or **46b** produced the isomerized *p*-naphthosemiquinones (**47,** Scheme IX). Semiquinones **47b–d** were also produced from the methoxyquinones electrolytically in DMF or DMSO (Scheme IX). In DMSO-d_6 the dideuterio derivative **47c** was formed. The elimination of methanol occurred so readily that the intermediate methoxy-1,4-semidiones (*i.e.,* **46c,d**) could not be detected. Without the benzo substituent the methoxysemidione was

Scheme IX



47a, $R_1 = R_2 = CH_3$; a^H = 2.25(2), 0.52(2), 0.26(2), 0.13(6) G
b, $R_1 = R_2 = C_6H_5$; a^H = 2.73(2), 0.70(2), 0.39(2) G
c, $R_1 = R_2 = C_6H_5$; a^H = 0.70(2), 0.35(2); a^D = 0.41(2) G
d, R_1 = H, $R_2 = C_6H_5$; a^H = 2.99, 2.78, 2.65, 0.72(2), 0.36(2) G

stable (**40c,d**) and no evidence of elimination was found, even in basic DMSO solution.

Experimental Section

General Preparation of Semidiones. The general techniques for the reductions with potassium *tert*-butoxide in dimethyl sulfoxide were followed as previously described.[10] Approximately 1-2 mg of a diketone in 0.5 ml of dry DMSO (distilled from calcium hydride) was placed in one side of an inverted U-cell[32] and potassium *tert*-butoxide (approximately 10 mg) was dissolved in 0.5 ml of dry DMSO in the other side. Both solutions were simultaneously deoxygenated with prepurified nitrogen for 15 min. The solutions were then mixed by inverting the cell, and the final solution was then shaken into a Varian Associates V-4548 aqueous solution sample cell.

The *in situ* electrolytic reductions were carried out in a flat cell with a mercury pool cathode and a platinum wire anode. Approximately 1-2 mg of an unsaturated diketone was dissolved in 1 ml of dry dimethylformamide containing 0.1 *M* tetra-*n*-butylammonium perchlorate as the electrolyte. This solution was placed inside the electrolytic cell and degassed with a stream of prepurified nitrogen for 15 min prior to the beginning of the electrolysis. Each electrolysis was carried out at the minimum voltage necessary to result in the production of a strong esr signal.

General Preparation of Benzosemiquinones from Semidiones. Air was allowed to enter the U-cell containing the DMSO solution of the semidione by separating the ground glass joints of the U-cell and flat cell for brief periods (5-10 sec). The solution was then shaken for 1-3 min and its esr spectrum was then monitored. The semidiones were completely converted to their corresponding semiquinones after this procedure had been repeated several times (in cases where a stable semiquinone resulted).

Complete Reduction of *syn*-7-Methylbicyclo[4.1.0]hept-3-ene-2,5-dione. The electrolysis was carried out in a specially constructed cell that had its anode and cathode compartments separated by a fine glass frit. A silver wire was used as the anode and a platinum wire as the cathode. Each wire was coiled and the coil was arranged in the shape of a circle such that the plane of the circle was parallel to the plane of the glass frit. The distance between the cathode and anode coils was 2 cm. The capacity of the anode compartment was approximately 2 ml and that of the cathode was approximately 3 ml. A portion of the contents of the cathode compartment could be drained through a stopcock into a flat cell which fitted into the esr cavity.

A solution of 1 mg of *syn*-7-methylbicyclo[4.1.0]hept-3-ene-2,5-dione was dissolved in 3 ml of dry dimethylformamide containing 54 mg of tetrabutylammonium iodide and placed in the cathode compartment. A solution of 36 mg of tetrabutylammonium iodide in 2 ml of dimethylformamide was placed in the anode compartment. These solutions were simultaneously degassed on a vacuum line in several freeze-thaw cycles. The electrolysis was carried out at the minimum negative voltage necessary to give the reddish brown color of the semidione forming at the surface of the cathode (−4 V). Initially the current was 0.5 mA but it dropped in value as the electrolysis proceeded and was nearly zero after 0.5 hr. The electrolysis was stopped at this point and a portion of the contents of the cathode was drained into the flat cell. The esr spectrum of this sample was then recorded in the normal fashion.

***anti*- and *syn*-12-Methyltetracyclo[4.4.0.$1^{3,4}$.$1^{7,10}$]dodec-8-ene-2,5-dione (19, R = Methyl).** A solution of 0.03 mol of diphenylsulfonium ethylide in 200 ml of dry 1,2-dimethoxyethane (distilled from lithium aluminum hydride) was prepared under nitrogen at −77° according to the precedure of Corey and Jautelat.[33] The ylide solution was warmed to −20° and a solution of 5.22 g (30 mmol) of tricyclo[4.4.0.$1^{7,10}$]undeca-3,8-diene-2,5-dione[12] (**18**) in 20 ml of dry 1,2-dimethoxyethane was added over 5 min to the rapidly stirred ylide solution. The intense yellow color of the ylide was discharged and the resulting solution turned blue near the end of the addition. The solution was stirred for 8 hr at −15 to −25° during which time the color changed to reddish brown.

The reaction mixture was poured into 500 ml of water and extracted with 600 ml of ether. The ether solution was washed with water (4 × 500 ml), dried over magnesium sulfate, and concentrated *in vacuo* affording 16.1 g of a brown oil.

The crude product was chromatographed on a 1 × 18 in. column of silica gel (60-200 mesh) slurry-packed in 3% ether-hexane. Fractions of 250 ml were collected: fraction 1, 3% ether-hexane, nil; 2, 3% ether-hexane, 5.70 g of diphenyl sulfide; 3 and 4, 6% ether-hexane, nil; 5 and 6, 12% ether-hexane, nil; 7, 20% ether-hexane, nil; 8 and 9, 20% ether-hexane, 343 mg of an unidentified solid; 10 and 11, 20% ether-hexane, 695 mg of an unidentified yellow oil; 12-22, 2.27 g (35%) of a mixture of *syn*- and *anti*-12-methyltetracyclo[4.4.0.$1^{3,4}$.$1^{7,10}$]dodec-8-ene-2,5-dione. Nmr analysis of the crude mixture showed that it contained 18% of the syn isomer and 82% of the anti isomer.

Crystallization of the mixture from ether-hexane afforded 1.16 g of pure *anti*-12-methyltetracyclo[4.4.0.$1^{3,4}$.$1^{7,10}$]dodec-8-ene-2,5-dione as white needles: mp 127-128°; ir(KBr) 1686 and 1675 (C=O); nmr ($CDCl_3$) δ 6.06 (t, 2, J = 1.6 Hz), 3.49-3.25 (m, 2), 3.25-3.07 (m, 2), 2.54-2.08 (m, 1), 1.98 (d, 2, J = 4.8 Hz), 1.55-1.07 and 1.26 (m and d, 5, J = 5.6 Hz); mass spectrum (70 eV) *m/e* 202 (parent ion).[34]

syn-12-Methyltetracyclo[4.4.0.$1^{3,4}$.$1^{7,10}$]dodec-8-ene-2,5-dione was not isolated in pure form. The mother liquor from the above crystallization was evaporated to dryness, and the resulting material consisting of a mixture of *syn*- and *anti*-12-methyltetracyclo[4.4.0.$1^{3,4}$.$1^{7,10}$]dodec-8-ene-2,5-dione was used directly in the next step.

***anti*-7-Methylbicyclo[4.1.0]hept-3-ene-2,5-dione (13, R = methyl).** A saturated solution containing 338 mg (1.67 mmol) of *anti*-12-methyltetracyclo[4.4.0.$1^{3,4}$.$1^{7,10}$]dodec-8-ene-2,5-dione in methylene chloride was injected in 50 μl portions into a 0.25 in. × 5 ft glpc column (15% DEGS, 200°, 80 cm^3/min flow) and the effluent yellow oil (217 mg) was collected. This material, which solidified upon scratching, was sublimed at 70° (1 mm) giving 200 mg (88%) of a pale yellow solid: mp 40.5-51°; ir (CCl_4) 1675, 1687 (C=O), and 1601 cm^{-1} (D=C); nmr ($CDCl_3$) 6.44 (d, 2, J = 0.8 Hz), 2.49-2.27 (m, 2), 2.27-1.83 (m, 1), and 1.33 (d, 3, J = 5.5 Hz); mass spectrum (70 eV) *m/e* (rel intensity) 136 (8) (molecular ion), 121 (8), 108 (5).[34]

***syn*-7-Methylbicyclo[4.1.0]hept-3-ene-2,5-dione (9, R = methyl).** A saturated solution containing 433 mg (2.14 mmol) of *anti*- and *syn*-12-methyltetracyclo[4.4.0.$1^{3,4}$.$1^{7,10}$]dodec-8-ene-2,5-dione (50:50 mixture by nmr) in methylene chloride was injected in 50-μl portions onto a 0.25 in. × 5 ft glpc column (15% XF-1150, 195°, 150 cm^3/min flow) and the effluent oil was collected (200 mg, 68%). Nmr analysis showed that the product consisted of a mixture of *syn*- and *anti*-bicyclo[4.1.0]hept-3-ene-2,5-dione (47 and 53%, respectively). The pure syn isomer (25 mg) was obtained by preparative glpc (0.25 in. × 5 ft 10% QF-1 column, 145°, 75

cm^3/min flow) in three passes. The retention times under these conditions were 11.5 min (syn) and 13.4 min (anti).

Pure *syn*-7-methylbicyclo[4.1.0]hept-3-ene-2,5-dione crystallized upon standing at room temperature affording a pale yellow solid: mp 60.0–60.5°; ir (CCl_4) 1676 (C=O) and 1602 cm^{-1} (C=C); nmr ($CDCl_3$) 6.63 (slightly split singlet, 2), 2.64–2.36)m, 2), 2.34–1.68 (m, 1), and 1.35 (d, 3, J = 5.7 Hz); mass spectrum (70 eV) *m/e* (rel intensity) 136 (12) (molecular ion), 121 (17), 108 (13).[34]

Diphenylmethylsulfonium Tetrafluoroborate. The procedure of Franzen, *et al.*,[35] was followed affording (81%) of a clear oil.

Tetracyclo[4.4.0.1^{3,4}.1^{7,10}]dodec-8-ene-2,5-dione (19, R = H). To a rapidly stirred suspension of diphenylmethylsulfonium tetrafluoroborate (5.34 g, 18.5 mmol) in 175 ml of dry tetrahydrofuran (distilled from lithium aluminum hydride) under nitrogen at −72° was added 14.85 ml (18.0 mmol) of *tert*-butyllithium in pentane (1.21 M) over 15 min. The resulting bright yellow solution was stirred for 0.5 hr. A solution of **18** in 12 ml of dry tetrahydrofuran was added over 5 min affording a blue solution. The solution was stirred at −72° for 21 hr and then at −30° for 3 hr. Water (3 ml) was slowly added at −30°. The reaction mixture was extracted with ether and the ether extract was washed with water and dried over magnesium sulfate. Concentration *in vacuo* afforded 6.87 g of a reddish brown oil.

The crude product was chromatographed on a 2.5 × 75 cm column of silica gel (60–200 mesh) slurry packed in hexane. Fractions of 250 ml were collected: fraction 1, hexane, nil; 2, hexane, 2.83 g of diphenyl sulfide; 3 and 4, hexane, nil; 5, 5% ether–hexane, nil; 6, 10% ether–hexane, nil; 7, 10% ether–hexane, nil; 8, 20% ether–hexane and 9–12, 30% ether–hexane, 928 mg of an unidentified yellow oil; 13 and 14, 30% ether–hexane, nil; 15, 40% ether–hexane, nil; 16–18, 40% ether–hexane, 569 mg of tetracyclo[4.4.0.1^{3,4}.1^{7,10}]dodec-8-ene-2,5-dione.

Fractions 16–18 were recrystallized twice from ether–hexane affording 315 mg (9%) of pale yellow crystals: mp 118–119.5°; ir (CCl_4) 1696 (C=O) and 1662 (C=C) cm^{-1}; nmr ($CDCl_3$) δ 6.17 (t, 2, J = 1.7 Hz), 3.59–3.36 (t, 2, J = 1.7 Hz), 3.35 (s, 2), 2.43–1.60 and 2.18 (m and s, 4), and 1.60–1.12 (m, 2); mass spectrum (70 eV) *m/e* 188 (molecular ion), 123, 92.[34]

Bicyclo[4.1.0]hept-3-ene-2,5-dione (9 or 13, R = H). A saturated solution containing 216 mg (1.15 mmol) of **19**, R = H, in methylene chloride was injected onto a glpc column (0.25 in. × 5 ft 15% Carbowax 20M, 190°, 80 cm^3/min flow) and the effluent oil was collected. This material was sublimed at 80° (0.3 mm) affording 84 mg (60%) of a pale yellow solid: mp 51–52°; ir (CCl_4) 1681 (C=O) and 1603 (C=C) cm^{-1}; nmr ($CDCl_3$) δ 6.44 (d, 2, J = 0.7 Hz), 2.76–2.41 (m, 2), and 2.00–1.57 (m, 2); mass spectrum (70 eV) *m/e* (rel intensity) 122 (15) (molecular ion), 94 (6), 68 (6).[34]

Tricyclo[4.4.0.1^{7,10}]undec-8-ene-2,5-dione Monoethylene Ketal. This compound was synthesized in a similar manner to that reported for its 4-phenyl derivative.[14] Tricyclo[4.4.0.1^{7,10}]undec-8-ene-2,5-dione[14] (28.7 g, 0.16 mol), ethylene glycol (10.1 g, 0.16 mol), *p*-toluenesulfonic acid (80 mg), and 380 ml of benzene were refluxed for 5.5 hr with stirring and with water collection in a Dean–Stark trap. The solution was cooled and 2.0 ml of pyridine was added to the stirred solution. The solution was washed with water, dried over magnesium sulfate, and concentrated *in vacuo* affording 34.1 g (95%) of a yellow liquid. This material was used in the next step without further purification.

Cyclohex-2-ene-1,4-dione Monoethylene Ketal (20). This compound was synthesized in a manner similar to that reported[14] for its 5-methyl and 5-phenyl derivatives. Tricyclo[4.4.0.1^{7,10}]undec-8-ene-2,5-dione monoethylene ketal (34.1 g, 0.16 mol) was rapidly distilled twice at 20 mm with the temperature held at 200°. A final distillation afforded a fraction (6.91 g, 29%) consisting of a clear liquid, bp 141–150° (20 Torr), which was greater than 97% pure by glpc.

The analytical sample was obtained by preparative glpc (0.25 in. × 5 ft 15% XF1150, 150°, 80 cm^3/min flow): nmr (CCl_4) δ 6.47 and 5.87 (q, 2, J = 10.2 Hz), 3.96 (s, 4), and 2.67–1.94 (m, 4); mass spectrum (70 eV) *m/e* (rel intensity) 154 (1) (molecular ion), 126 (18), 110 (5).[34]

Irradiation Apparatus. The photolyses described below were conducted in Pyrex vessel constructed from 6 and 7 cm Pyrex tubing (which formed respectively the inner and outer walls of the vessel). The vessel was 26 cm in length and had a capacity of ~ 150 ml. The vessel was completely enclosed except for a small side arm on the side near the top (constructed from 1 cm Pyrex tubing) through which the reactants were introduced and at which the entire vessel could be sealed off *in vacuo*. A regular Hanovia immersion well containing a 550-W medium pressure mercury lamp was placed inside the portion of the vessel constructed from the 6-cm tubing. The entire apparatus was placed in a 3-l. beaker of water which was cooled by means of cold water circulating through a 0.25 in. × 10 ft copper coil immersed in the beaker.

7,8-Dimethylbicyclo[4.2.0]oct-7-ene-2,5-dione Monoethylene Ketal (24). Cyclohex-2-ene-1,4-dione monoethylene ketal (1.8 g, 11.7 mmol) in 40 ml of 2-butyne was irradiated for 4 hr in the apparatus described. Distillation of the 2-butyne afforded 2.05 g (97%) of a clear liquid.

The analytical sample was obtained by preparative glpc (10% QF-1, 175°, 75 cm^3/min flow): ir (neat) 1691 (C=O) cm^{-1}; pmr (CCl_4) 3.93 (s, 4), 3.05–1.77 (m, 4), and 1.77–1.50 (m, 6); mass spectrum (70 eV) *m/e* 208 (molecular ion), 122, 100.[34]

7,8-Dimethylbicyclo[4.2.0]oct-7-ene-2,5-dione (25b). A solution of 0.50 g (2.40 mmol) of **24** in 5 ml of dioxane and 5 ml of 3% sulfuric acid was stirred at 25° for 4 hr. The solution was poured into 100 ml of water and extracted with 100 ml of ether. The ether extract was washed twice with 100 ml of 5% sodium bicarbonate solution, dried over magnesium sulfate, and concentrated *in vacuo* giving 220 mg of a yellow liquid. Glpc analysis showed that this material consisted of a 40:60 mixture of **25** and **24.**

7,8-Dimethylbicyclo[4.2.0]oct-7-ene-2,5-dione (60 mg, 15%) was isolated as a pale yellow liquid by preparative glpc (10% QF-1, 170°, 80 cm^3/min flow): ir (neat) 1706 (C=O) cm^{-1}; nmr (CCl_4) δ 3.31 (s, 2), 2.75–2.45 (m, 4), and 1.66 (s, 6); mass spectrum (70 eV) *m/e* (real intensity) 164 (10) (molecular ion), 146 (3), 136 (4).[34]

7,8-Dimethylbicyclo[4.2.0]octane-2,5-dione Monoethylene Ketal (26). A solution of 3.00 g (19.4 mmol) of **20** in 100 ml of *cis*-2-butene was sealed in the photolysis vessel (described above) at 0.4 mm and irradiated for 5.5 hr. Distillation of the excess *cis*-2-butene afforded 3.90 g (96%) of a colorless liquid. Glpc analysis revealed that starting material was absent and that the product consisted of three components (presumed to be isomers). This material was used without further purification in the next step.

***cis*-7,8-Dimethylbicyclo[4.2.0]octane-2,5-dione (14b = 14S or 14A, R$_1$ = R$_2$ = CH$_3$, R$_3$ = H) and *anti,syn*-7,8-dimethylbicyclo[4.2.0]octane-2,5-dione (14c, R$_1$ = R$_3$ = CH$_3$, R$_2$ = H).** A solution of 2.00 g (9.52 mmol) of 7,8-dimethylbicyclo[4.2.0]octane-2,5-dione monoethylene ketal (mixture of isomers from above) dissolved in 18 ml of dioxane and 18 ml of 3% sulfuric acid was stirred at 25° for 3.7 hr. The solution was poured into 100 ml of water and the mixture was extracted twice with ether (100 ml). The ether solution was washed with 5% sodium bicarbonate (2 × 100 ml) and dried over magnesium sulfate. Concentration *in vacuo* afforded 940 mg (59%) of a mixture of 39% *syn,anti*-7,8-dimethylbicyclo[4.2.0]octane-2,5-dione and 61% of the *cis*-7,8-dimethylbicyclo[4.2.0]octane-2,5-dione as determined by glpc analysis.

The two isomers were separated by preparative glpc (5 ft × 0.25 in. 20% Hallcomid column, 150°, 80 cm^3/min flow).

syn,anti-7,8-Dimethylbicyclo[4.2.0]octane-2,5-dione has a retention time of 41 min under these conditions and was obtained as a clear liquid which solidified upon standing in the freezer: ir (neat) 1703 cm^{-1} (C=O); nmr ($CDCl_3$) δ 3.43–1.91 and 2.75 (m and s, 8), 1.41–1.14 (m, 3), and 1.14–0.82 (m, 3); mass spectrum (50 eV) *m/e* calcd for $C_{10}H_{14}O_2$, 166.0994; found, 166.1005.[36]

cis-7,8-Dimethylbicyclo[4.2.0]octane-2,5-dione had a retention time of 48.6 min under these conditions and was obtained as a clear liquid: ir (neat) 1702 cm^{-1} (C=O); nmr ($CDCl_3$) δ 3.00–D.56 and 2.78 (m and s, 8) and 1.36–0.79 (m, 6); mass spectrum (50 eV) *m/e* calcd for $C_{10}H_{14}O_2$, 166.0994; found, 166.1010.[36]

***cis*-7,8-Dimethylbicyclo[4.2.0]octane-2,5-dione (14b = 14S or 14A, R$_1$ = R$_2$ = CH$_3$, R$_3$ = H).** A mixture of 61 mg (0.37 mmol) of **25**, 18 mg of 10% palladium on charcoal, and 4 ml of methyl alcohol was hydrogenated at 25 psi for 15 min. The mixture was filtered and concentrated *in vacuo* affording 65 mg of a clear oil which showed both C=O and OH bands in the ir. Glpc analysis of the oil showed that it consisted of at least four components.

The pure *cis*-7,8-dimethylbicyclo[4.2.0]octane-2,5-dione (11.0 mg, 18%) was isolated as a colorless liquid by preparative glpc (5 ft

× 0.25 in. 15% Carbowax 20M, 150°, 80 cm³/min flow, R_f = 13.3 min): ir (neat) 1698 cm⁻¹ (C=O); nmr ($CDCl_3$) δ 3.54–2.83 (m, 4), 2.72 (s, 4), and 1.13–0.87 (m, 6); mass spectrum (50 eV) *m/e* calcd for $C_{10}H_{14}O_2$, 166.0994; found, 166.0994.[36] This isomer yielded **37d** immediately upon oxidation. It is believed to be most likely the anti,anti isomer (**14A**).

7,8-Dichlorobicyclo[4.2.0]octane-2,5-dione Monoethylene Ketal (21). A solution of 3.00 g (19.5 mmol) of **20** and 120 ml of 1,2-dichloroethylene (cis and trans mixture) was irradiated in the apparatus described above for 2 hr. Distillation of the excess dichloroethylene afforded 4.75 g (97%) of 7,8-dichlorobicyclo[4.2.0]octane-2,5-dione monoethylene ketal (**22**) as an orange-brown oil. This material was used without further purification in the next step: pmr ($CDCl_3$) δ 4.84–4.25 (m, 2), 4.16–3.87 (m, 4), 3.44–3.26 (m, 2), and 2.74–1.92 (m, 4).

7,8-Dichlorobicyclo[4.2.0]octane-2,5-dione Bisethylene Ketal (22). 7,8-Dichlorobicyclo[4.2.0]octane-2,5-dione monoethylene ketal (2.51 g, 10.0 mmol), ethylene glycol (930 mg, 15.0 mmol), *p*-toluenesulfonic acid (5 mg), and benzene (25 ml) were refluxed for 5 hr during which time the water formed was collected in a Dean–Stark trap. The solution was cooled and pyridine (0.3 ml) was added with stirring. Water (200 ml) was added and the mixture was extracted with ether. The extract was washed with water and dried over magnesium sulfate. Concentration *in vacuo* afforded 2.56 g (87%) of **22** as an orange-red oil. This material was used without further purification in the next step: pmr ($CDCl_3$) δ 4.73–4.29 (m, 2), 4.11–3.73 (m, 8), 3.04–2.91 (m, 2), and 2.07–1.46 (m, 4); mass spectrum (70 eV) *m/e* (real intensity) 261 (1), 259 (3).

Bicyclo[4.2.0]octane-2,5-dione Bisethylene Ketal (23). A suspension of 0.64 g (92 mg-atom) of finely chopped lithium wire in 20 ml of tetrahydrofuran was added to a stirred solution of 2.56 g (8.7 mmol) of **22** and 4.25 g (57.4 mmol) of *tert*-butyl alcohol in 45 ml of dry tetrahydrofuran (dried over molecular seives). The reaction mixture was stirred for 30 min during which time slight warming occurred and the color turned to brown. The reaction mixture was refluxed for 2 hr and then stirred at 25° for 2 hr. The reaction mixture was decanted from the excess lithium into 50 ml of methyl alcohol, and ice was slowly added to the solution after the hydrogen evolution had ceased. The product was extracted with ether, and the extract was washed with water and dried over magnesium sulfate. Concentration *in vacuo* afforded 1.26 g of a yellow brown oil.

Crystallization from ethyl ether at −77° afforded 850 mg (43%) of a white solid: mp 45–46°; nmr ($CDCl_3$) δ 3.90 (s, 8), 2.76–2.35 (m, 2), and 2.13–1.46 (m, 8); mass spectrum (70 eV) *m/e* (rel intensity) 226 (3), 181 (8), and 183 (9).[34]

Bicyclo[4.2.0]octane-2,5-dione (14a, $R_1 = R_2 = R_3 = H$). A solution of 0.7 g (3.10 mmol) of **23** in 8 ml of dioxane and 6 ml of 3% sulfuric acid was stirred at room temperature for 3.5 hr. The reaction mixture was poured into 100 ml of water and extracted with ether (3 × 50 ml). The ether extract was washed with 5% sodium bicarbonate (2 × 50 ml) and water (2 × 50 ml) and dried over magnesium sulfate. Concentration *in vacuo* afforded 1717 mg of a yellow oil. Bicyclo[4.2.0]octane-2,5-dione (6.0 mg, 1.4%) was isolated from this crude mixture as a colorless liquid by preparative glpc (5 ft × 0.25 in. 15% Carbowax 20M, 175°, 80 cm³/min flow, R_t = 4.8 min): mass spectrum (50 eV) calcd for $C_8H_{10}O_2$, 138.0681; found, 138.0686.

***Bicyclo[4.2.0]oct-7-ene-2,5-dione* (25a).** To a filtered solution of sodium naphthalide prepared by stirring 3.3 g (144 mmol) of sodium with 17.5 g (137 mmol) of naphthalene for 28 hr in 450 ml of DME under nitrogen was added 3.1 g (10.5 mmol) of **22** in 50 ml of DME over a 2-hr period. The solution was stirred an additional 45 min before flushing with oxygen until the solution became orange. The solvent was removed under reduced pressure to give a red solid from which the bisethylene ketal of **25a** could be isolated by chromatography on silica gel and vacuum distillation (bp 113°, 1.2 Torr).

The crude dehalogenated product was dissolved in 500 ml of ether and stirred with 500 ml of 3 *N* hydrochloric acid under nitrogen for 1.5 hr at 25°. The aqueous layer was extracted with ether, and the combined ethereal solutions were washed with saturated aqueous sodium bicarbonate and dried ($MgSO_4$). Distillation of the ether under reduced pressure gave a yellow solid which was dissolved in ethyl acetate (5%)-benzene (95%) and chromatographed on silica gel. Naphthalene was eluted with pentane. The desired product, contaminated with polymeric material, was eluted with ethyl acetate (5%)-benzene (95%). The solvent was removed and 300 mg of **25a** (21%) was obtained by dissolving the residue in a minimum amount of carbon tetrachloride, pouring into 200 ml of pentane, and filtering to remove the insoluble material.

Purification by glpc (5% Carbowax column at 150°) gave material with: ir (neat) 1713, 1309, 1268, 1174, 818, 762, 682 cm⁻¹; pmr ($CDCl_3$) δ 6.36 (s, 2), 3.82 (s, 2), 2.32–3.32 (m, 4); mass spectrum (MS-902) 136.0524, calcd for $C_8H_8O_2$ 136.0524.

7,8-Dimethyl-3,4-benzobicyclo[4.2.0]octa-3,7-diene-2,5-dione (precursor to 46a). Sublimed naphthoquinone (3.16 g) and 2-butyne (6.2 ml) were dissolved in 250 ml of benzene in a Vycor flask equipped with a cooling coil, magnetic stirrer, and septum. The solution was irradiated for 44 hr with a 275-W sunlamp. Removal of the benzene under vacuum left a solid which was eluted from a silica gel column by ethyl acetate (5%)-CCl_4 (95%) to give 5% of material with mp 116–117° after sublimation (0.04 Torr), lit.[37] mp 120–121°: pmr ($CDCl_3$) δ 8.16–7.55 (m, 4) 3.82 (m, 2), 1.66 (d, 6, J = 1.5 Hz); mass spectrum (70 eV) gave the parent ion at *m/e* 212.

Other Reagents. 7,8-Diphenyl-3,4-benzobicyclo[4.2.0]octa-3,7-diene-2,5-dione[38] (precursor to **46b**), 1-methoxy-7,8-diphenyl-3,4-benzobicyclo[4.2.0]octa-3,7-diene-2,5-dione, and 1-methoxy-8-phenyl-3,4-benzobicyclo[4.2.0]octa-3,7-diene-2,5-dione were kindly supplied by Professor Pappas.[29] 1,3,4,6-Tetramethylbicyclo[4.1.0]hept-3-ene-2,5-dione[39] (precursor to **27d**) and 1,3-di-*tert*-butylbicyclo[4.1.0]hept-3-ene-2,5-dione[40] (precursor to **27e**) were prepared according to the literature. 3,7,7-Trimethylbicyclo[4.1.0]hept-3-ene-2,5-dione[7] and eucarvone (precursors to **27f**) have been described[9] as have been 6,6-dimethylcyclohept-2-ene-1,4-dione (precursor to **27i**),[9] 3,4-benzobicyclo[4.1.0]hept-3-en-2-one, and 2,3-benzocyclohepta-2,4-dienone (precursors to **27j**).[9] 4,7,7-Trideuterioeucarvone[41] (precursor to **27g**) was prepared by reaction of eucarvone with sodium methoxide in CH_3OD at 25° for 24 hr: pmr (CCl_4) δ 6.35 (broad s, 1), 5.9 (broad s, 1), 1.9 (d, 3), 1.1 (s, 6); mass spectrum (70 eV) *m/e* 153 (parent ion), 138, 128, 110, 93. Oxidation in DMSO-d_6 yielded **27g**. 1,1,4-Trimethylcyclohepta-2,4-dien-6-one was prepared according to the literature.[42] Material purified by glpc (15% QF-1) column at 150° had pmr (CCl_4) δ 1.09 (s, 6), 2.0 (d, 3, J = 1.5 Hz), 2.48 (s, 2 H), 5.5–6.1 (m, 3). The photodimer of 2,3-dimethyl-*p*-benzoquinone was prepared according to the literature,[43] mp 162–163°.

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A New Ring System. 2,6-Dioxabicyclo[2.2.2]octane, a Highly Reactive Bicyclic Acetal

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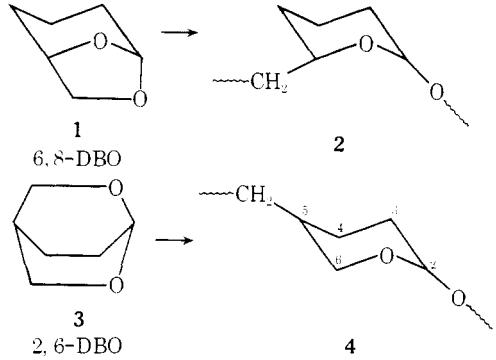
Abstract: A convenient synthesis of 2,6-dioxabicyclo[2.2.2]octane (**3**), the parent compound of a new ring system, has been worked out. This bicyclic acetal is highly reactive, oligomerizing in the solid phase at room temperature and hydrolyzing several orders of magnitude faster than related model compounds. Lewis and proton acids readily polymerized **3** to the 1,4-pyranose homopolymer **4**, η_{inh} 0.13–1.1. Stereoregular propagation by SN2 displacement on the bicyclic oxonium ion occurred at low temperatures using fluro acids as initiators. Stereorandom propagation by SN1 reaction of an intermediate carbonium ion was observed at +28° with methanesulfonic or trifluoroacetic acid initiation. The stereochemistries of the polymers obtained under these conditions agreed well with those calculated from conformational considerations for the limiting cases.

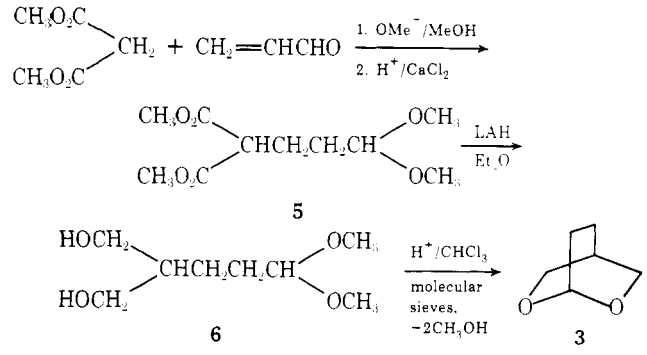
The understanding and chemical synthesis of polysaccharides are of great biomedical interest.[1] The synthesis of stereoregular polysaccharides has been a subject of vigorous study in our laboratories and elsewhere. A stereoregular substituted polysaccharide from 1,6-anhydro-2,3,4-tri-*O*-methyl-β-D-glucopyranose was initially reported by Korshak[2] and Schuerch.[3] Later work by Schuerch and coworkers reported other substituted polysaccharides.[3] Most recently, attention has turned toward the synthesis of polysaccharide analogs *via* ring-opening polymerization of unsubstituted bicyclic acetals. Specifically, the cationic ring-opening polymerization of 6,8-dioxabicyclo[3.2.1]octane (6,8-DBO) (**1**) has been shown to proceed at low temperatures *via* a direct displacement-type propagation step to give a completely stereoregular 1,3-linked tetrahydropyranoside **2**.[4-6] We now report the synthesis and ring-opening polymerization of 2,6-dioxabicyclo[2.2.2]octane (**3**) to give the 1,4-linked analog **4**.



Results

Synthesis. The synthesis of **3** was achieved as described in Scheme I. The synthesis of the required intermediate **6** paralleled that used by earlier workers[7,8] to prepare the analogous diethyl acetal. Michael addition of sodio dimethyl malonate to acrolein with subsequent acetalization *in situ* gave **5** in 50% yield. Reduction of **5** with lithium aluminum hydride gave a high yield of **6**. The diol acetal, **6**, underwent

Scheme I



intramolecular acid-catalyzed acetal exchange in dilute chloroform solution to afford the camphoraceous bicyclic acetal **3** in up to 35% yield. The monomer proved to be hygroscopic and unstable toward oligomerization under ordinary conditions and had to be stored under nitrogen at Dry Ice temperatures.