Application of Electron Spin Resonance Spectroscopy to Studies of Valence Isomerization. 6. Bicyclo[4.2.0]octa-3,7-diene-2,5-semidiones[1]

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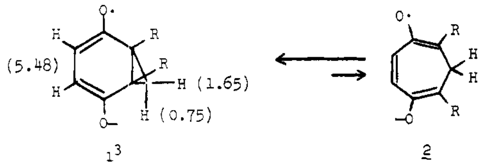
It is demonstrated that bicyclo[4.2.0]octa-3,7-diene-2,5-semidione is a more stable valence isomer than the monocyclic 2,5,7-cyclooctatriene-1,4-semidione. Oxidative decarbonylations in basic solution to yield *p*-benzosemiquinones are reported for the 2,5,7-cyclooctatriene-1,4-dione and 3,6-cycloheptadiene-1,2,5-trione systems. Rearrangement of bicyclo[4.2.0]oct-7-ene-2,5-semidiones to the *p*-semiquinones of benzocyclobutane is catalyzed by oxygen, and it is postulated that the reaction proceeds via a chain process involving the *p*-quinone of benzocyclobutene.

We have previously demonstrated by ESR spectroscopy that bicyclo[4.1.0]hept-3-ene-2,5-semidione is the preferred valence isomer rather than cyclohepta-1,3,5-triene-2,5-semidione.[2] The structural assignment is easily made by a comparison of the hfsc for **1** with R = H and R = CH_3. For the monocyclic structure **2**, the values of $a_{R=H}{}^H$ and $a_{R=CH_3}{}^H$ should be nearly the same, since when hydrogen or methyl is attached to an sp^2 carbon with spin density, $Q_{\dot{C}H}{}^H = -23$ G and $Q_{\dot{C}CH_3}{}^H = +28$ G.[3] When methyl is substituted for hydrogen at the 1,6 position in **1**, we observe $a_{CH_3}{}^H = 0.25$ G, which is a significant decrease from $a^H = 3.01$ G for the parent system. Thus, the bicyclic structure is demanded for the semidione. The equilibrium between **1** and **2** greatly favors **1**, presumably because the semidione reflects the stability of the parent dione. The bicyclic enedione which is a precursor to **1** is a stable structure, whereas a covalent structure cannot be drawn for the monocyclic dione.



1[3]

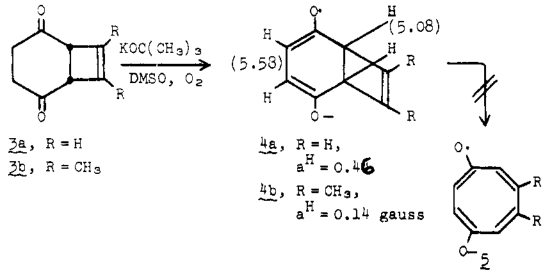
R = H, a^H = 3.01 gauss

R = CH_3, $a^H_{CH_3}$ = 0.25 gauss

2

(not detected)

We have also reported bicyclo[4.2.0]octa-3,7-diene-2,5-semidiones (**4**) prepared by the oxidation in basic solution of bicyclo[4.2.0]oct-7-ene-2,5-dione (**3**) or by reduction of substituted bicyclo[4.2.0]octa-3,7-diene-2,5-diones.[2,5] The bicyclic structure seems secure on the basis of the similarity of hfs between **1** and **4**, as well as the appreciable difference between $a_H{}^H$ and $a_{CH_3}{}^H$ for the 7,8 substituents. Examples of **4** with methyl at the bridgehead positions have not been synthesized. However, we have examined bridgehead substitution for the benzo derivatives, **7**. Table I presents the observed hfsc for several substitution patterns in **7**. All of the data are consistent with the structure assigned to **7** and are consistent with the observed hfsc for **4**.



3a, R = H

3b, R = CH_3

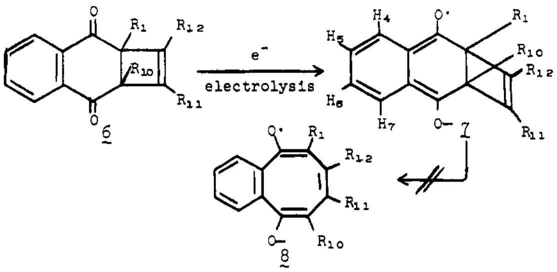
4a, R = H, a^H = 0.46

4b, R = CH_3, a^H = 0.14 gauss

5

not detected

The assignment of hfsc to $H_{4,7}$ (small) and $H_{5,6}$ (large) was by analogy to semidiones **9**.[6] Semidione **7c** with a bridgehead methyl was observed only as a transient species, while semidione **7d** could not be observed at all. Instead, 2,3-dimethyl-1,4-naphthosemiquinone (**10**) was formed, presumably via a cycloreversion process of the semidione or possibly of the analogous dianion. Reduction of diones **6e** and **6f** gave the semiquinone resulting from the loss of methanol and hydrogenation of the cyclobutene ring. The formation of this product is considered below.

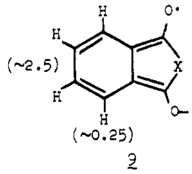


6

7

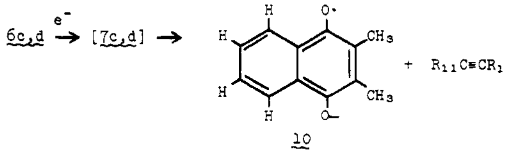
8

not detected



9

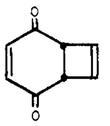
X = O, S, NH, CH_2, $CHCH_3$



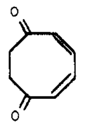
10

a^H = 0.35(2), 0.71(2), 2.48(6) gauss

In order to ascertain if **4** is indeed the preferred valence isomer relative to **5** and if a rapid isomerization of **5** to **4** occurs, we have studied the formation of semidiones from the unsubstituted bicyclic bicyclo[4.2.0]octa-3,7-diene-2,5-dione (**11**) via reduction, from 2,4-cyclooctadiene-1,6-dione (**12**) via oxidation, and from 2,5,7-cyclooctatriene-1,4-dione (**13**) via reduction. Reduction of **11** by basic DMSO[7] or electrolytically in DMSO yielded **4a** with no indication of **5**, but only when the system had been scrupulously deoxygenated (Figure 1a). In the presence of traces of oxygen, **4a** was isomerized to the



11



12

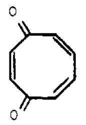


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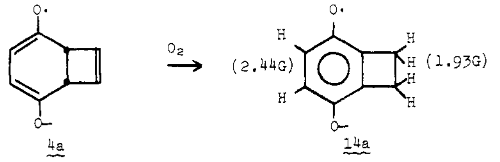
Table I. Observed Hfsc (G) for 7 (DMSO, 25 °C)

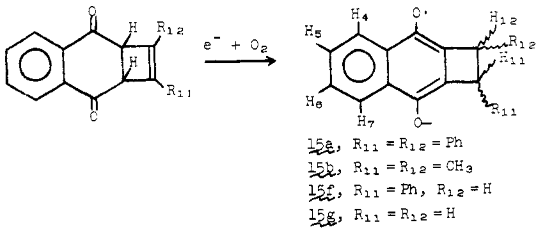
		substituents				a^H				
registry no.	precursor	R_1	R_{10}	R_{11}	R_{12}	$H_{4,7}$	$H_{5,6}$	$H_{1,10}$	registry no.	$H_{11,12}$
21399-85-9	**6a**	H	H	Ph	Ph	<0.3	2.33	6.02	54388-86-2	
21399-82-6	**6b**	H	H	CH_3	CH_3	0.2	2.48	5.43	54338-85-1	0.20[a]
21399-93-9	**6c**	CH_3	CH_3	Ph	H		2.20[b]		66609-88-9	
21441-73-6	**6d**	CH_3	CH_3	CH_3	CH_3	only **10**[c] obsd				
66562-75-2	**6e**	CH_3O	H	Ph	Ph	only **15a**[c] obsd				
66562-76-3	**6f**	CH_3O	H	Ph	H	only **16f**[c] obsd				

[a] $a_{CH_3}^H$. [b] Transient. [c] Registry no.: **10**, 66562-77-4; **15a**, 66673-24-3; **16f**, 66562-78-5.

p-benzosemiquinone **14a** in a catalytic process (Figure 1b). A similar isomerization catalyzed by oxygen was observed for

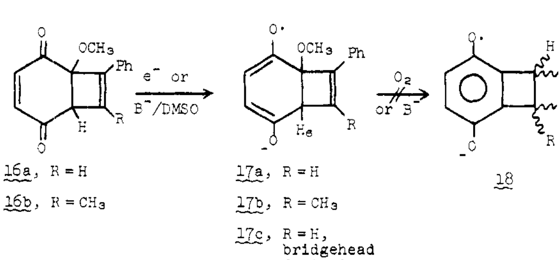


the benzo derivatives **6a,b** to give **15a,b** upon electrolytic reduction in the presence of traces of oxygen. Moreover, **6e** and



6f with a methoxy substituent at the bridgehead yielded **15a** and **15f**, respectively, as the only detectable radical anions upon electrolytic reduction or treatment with potassium *tert*-butoxide in DMSO solution. The hfsc of **15** are listed in Table II and compare favorably with the constants reported for **15g**.[8]

The conversion of **6e** and **6f** to the corresponding semiquinones **15** was somewhat surprising, because we had previously observed that a similar conversion does not occur for **16** which can be electrolytically reduced, or reduced by basic DMSO to **17** with no indication of the formation of **18**.[2] In



basic DMSO-d_6, **17a** undergoes hydrogen–deuterium exchange at the bridgehead position to form **17c**, but gives no indication of the elimination of methanol. The hfsc for **17a–c** are given in Table III.

The formation of **15** from **6**, or **14a** from **11**, suggests an elimination mechanism (**6e,f**) or oxidative dehydrogenation (**6a, 6b, 11**) to yield a benzocyclobutene derivative, as shown in Scheme I.

In the event that the intermediate cyclobutadiene derivative abstracts two hydrogen atoms from the starting dihydroquinones (**6a,b** and **11**), the isomerization (parts b and c of Scheme I) will be catalyzed by traces of oxygen. Such a reaction might be expected to transfer the bridgehead hydrogen atoms in a stereoselective cis manner to C-7,8. We have previously reported that **14b** and **14c** prepared from the appro-

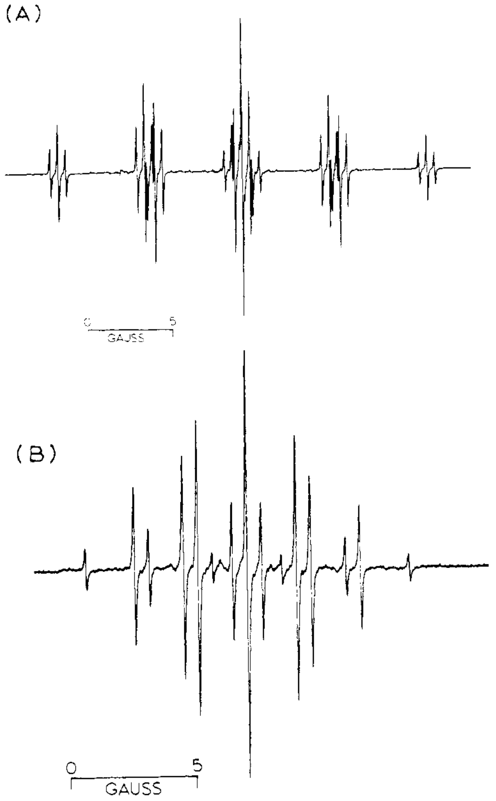


Figure 1. ESR spectra of (A) bicyclo[4.2.0]octa-3,7-diene-2,5-semidione (**4a**) in DMSO and (B) bicyclo[4.2.0]octa-3,6(1)-diene-2,5-semiquinone (**14a**) prepared by oxidation of a solution yielding spectrum (A).

Table II. Observed Hfsc (G) for 15 (DMSO, 25 °C)

	substituents		a^H			
precursor	R_{11}	R_{12}	$H_{4,7}$	$H_{5,6}$	$H_{11,12}$	other
15g[a]	H	H	0.44	0.75	2.94	
15a	Ph	Ph	0.33	0.63	2.70	
15b	CH_3	CH_3	0.26	0.52	2.25	0.13 (6 H)
15f	Ph	H	0.36	0.72	2.99 2.78 2.65	

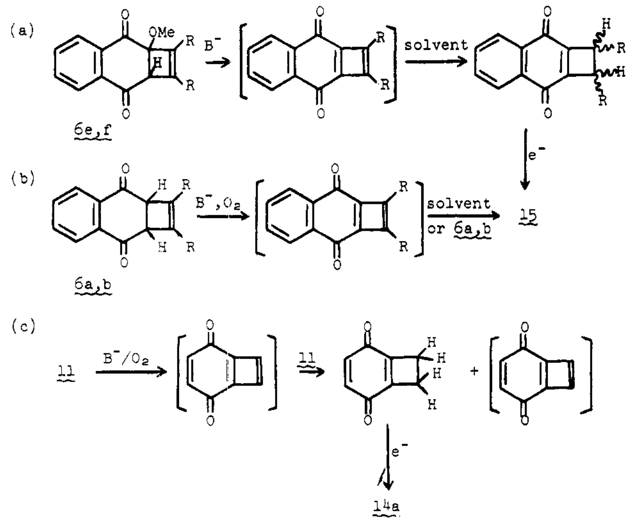
[a] Reference 8.

Table III. Observed Hfsc (G) for 17 (DMSO, 25 °C)

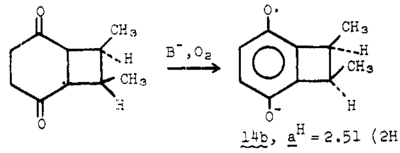
			a^H		
registry no.	precursor	R	$H_{4,5}$	H_6	R
54338-68-0	**17a**	H	5.58, 5.05	4.68	0.23 (1 H)
54338-69-1	**17b**	CH_3	5.65, 5.10	4.70	0.49 (3 H)
66562-79-6	**17c**	H[a]	5.62, 5.12	a^D = 0.70	0.21 (1 H)

[a] Bridgehead deuterium.

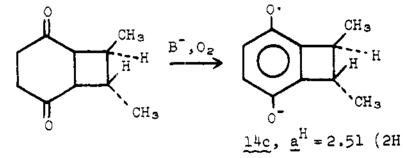
Scheme I



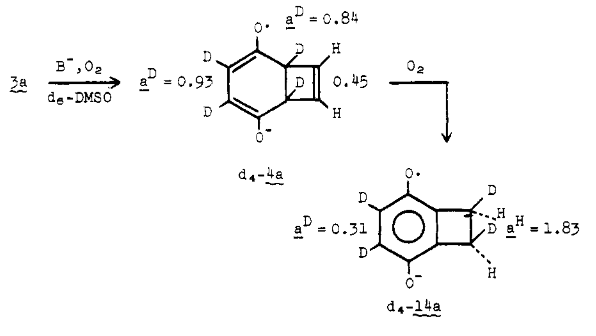
priate precursors have different ESR spectra and are not interconverted in basic solution.[2] The prediction of stereochemical control in the isomerization product was confirmed by the observation that **3b**, when treated with excess oxygen in DMSO solution, yielded only a single *p*-benzocyclobutane semiquinone and that this semidione possessed the stereochemistry of **14b** and not **14c**.[c] In a similar fashion, when **3a** was treated with oxygen in basic DMSO-d_6 solution the tetradeuterio derivative of **4a** was first formed, but excess oxygen led to the formation of the tetradeuterio derivative of **14a**, presumably with the cis stereochemistry.



14b, $a^H = 2.51$ (2H), 1.77 (2H) gauss

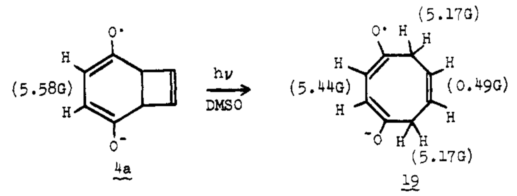


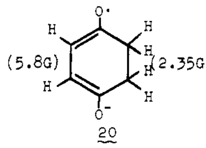
14c, $a^H = 2.51$ (2H), 1.71 (2H) gauss



Treatment of bicyclo[4.2.0]oct-7-ene-2,5-diones (**3**) with deficient quantities of oxygen in basic solution gives **4** with little interference from **14**. The dianion of the enedione apparently is a good trap for oxygen, which decreases the probability of the further oxidation to the postulated cyclobutadiene intermediate unless excess oxygen is employed.

Photolysis of the mixture of **11** and **4a** in DMSO/potassium *tert*-butoxide was investigated as a possible route to **5**. Irradiation with UV through silica produced a new semidione possessing hfs by eight hydrogen atoms. The multiplicities suggest a symmetric structure which we postulate to be **19**. The hfs of H-2,3 are quite close to that observed in other 1,4-semidiones, including **4**, **20**,[9] and **21**.[9] The hfs of the methylene groups in **19** are considerably greater than in **20** or **21**, perhaps because of conformational effects (two rapidly time-averaged conformations for **19**, a single rigid conformation for **20** or **21**). To exclude the alternative structure **22**, we investigated the reduction of the dienenedione **12**. Since electrolytic reduction of **12**, or treatment of **12** with deoxygenated DMSO containing potassium *tert*-butoxide, failed to produce a radical ion, we believe that **22** cannot be the structure of the above-mentioned photoreduction. Treatment of **12** with base and oxygen in DMSO did produce semidiones, but only bicyclic semidiones. One of the semidiones was **4a** and the other semidione had nearly identical hfsc to **4a** but with one bridgehead hydrogen missing. The hfsc were nearly the same as **17a**, suggesting structure **23** for the new semidione.





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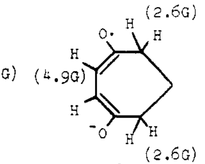

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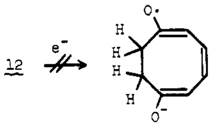

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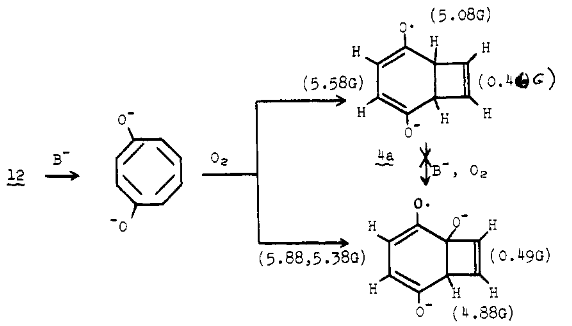
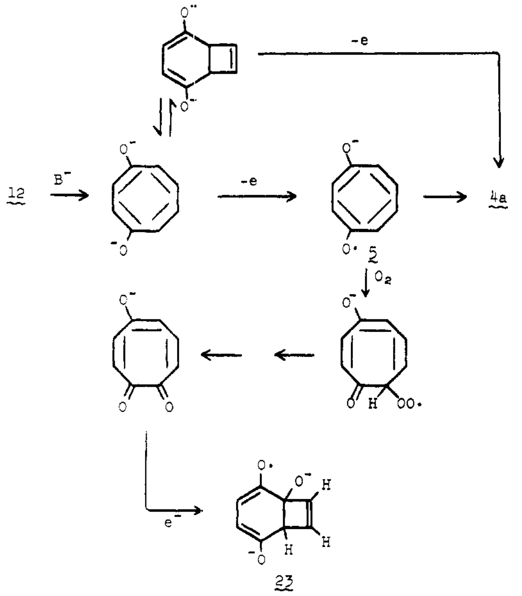


The formation of **4a** may occur via valance isomerization of the monocyclic dianion to the bicyclic dianion, followed by loss of an electron, or alternately by the loss of an electron from the monocyclic dianion followed by monocyclic–bicyclic valence isomerization (Scheme II). However, the results are strongly suggestive that **5** is thermodynamically less stable than **4a**. The semidione **23** is not observed upon oxidation of **3**, **4a**, or **11**. The formation of **23** can be easily rationalized if the monocyclic radical anion (Scheme II) is oxygenated prior to the monocyclic–bicyclic valence isomerization. Further oxygenation of the reaction mixture destroys **4a** and **23** and yields an ESR spectrum of *p*-benzosemiquinone whose formation will be discussed later.

2,5,7-Cyclooctatriene-1,4-dione[10] (**13**) decomposed rapidly in DMSO or DMF solutions. In acetonitrile the trienedione appeared stable, but no resolved ESR signals could be observed upon electrolytic reduction (mercury pool) or in tetrahydrofuran (platinum, −40 °C) or upon treatment with potassium *tert*-butoxide in DMSO. Dc polarography of the trienedione in acetonitrile with *tert*-butylammonium perchlorate (0.1 M) gave a single two-electron reduction with $E_{1/2}$

Scheme II



= −1.00 V (vs. SCE). From this we conclude that the radical anion is more easily reduced than the starting dione and this, connected with the instability of the parent dione, makes the detection of any radical ion (monocyclic or bicyclic) difficult when the trienedione is used as a processor. Nevertheless, the bicyclic radical ion **4a** is quite stable when prepared from a bicyclic precursor, and the absence of **4a** upon electrolytic reduction of the trienedione places some limit on the rate of the monocyclic → bicyclic valence isomerization of the as yet undetected **5** (Scheme III).

It was thus expected that treatment of **13** with basic DMSO should result in reduction to the dianion, which upon oxygenation should lead to **4a** and/or **23**. However, the only paramagnetic product we have been able to detect in this oxygenation is *p*-benzosemiquinone. *p*-Benzosemiquinone is also formed in the oxygenation of **12** and in the oxygenation of 5-hydroxy-α-tropolone in basic DMSO. Both of the ring contractions are apparently of the benzylic acid type, which has been previously observed in semidione systems.[11] The formation of *p*-benzosemiquinone from either 5-hydroxy-α-tropolone, **12**, or **13** upon oxygenation in basic DMSO solution undoubtedly follows the general outline of Scheme IV. *p*-Troposemiquinone (**24**)[12] can be detected in the oxidation of 5-hydroxy-α-tropolone with deficient oxygen in DMSO-containing potassium *tert*-butoxide. If the oxidation of 5-hydroxy-α-tropolone is conducted in the presence of hydroxide ions in DMSO, the observed semiquinone is the one derived from 1,2,4-trihydroxybenzene.[13] Apparently, under these conditions *p*-tropoquinone is hydroxylated or oxygenated to a tetraoxygenated species which then yields the trioxysemiquinone by the benzylic acid rearrangement sequence (Scheme V). The semiquinone of 1,2,4-trihydroxybenzene cannot be formed by the hydroxylation or oxygenation of *p*-benzosemiquinone under the reaction conditions.

Scheme III

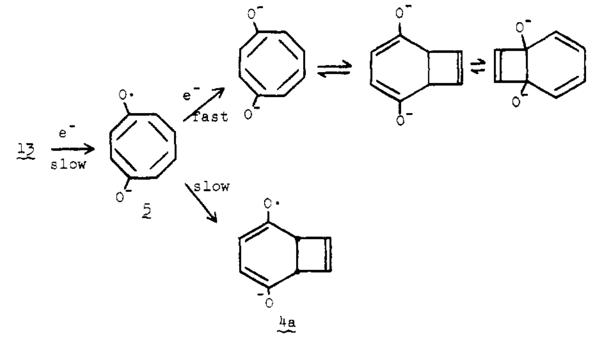
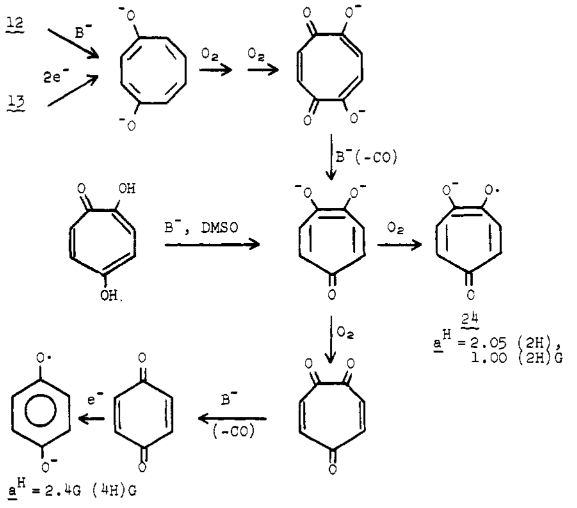


Table IV. McLachlan Spin Density Calculations for 24[a]

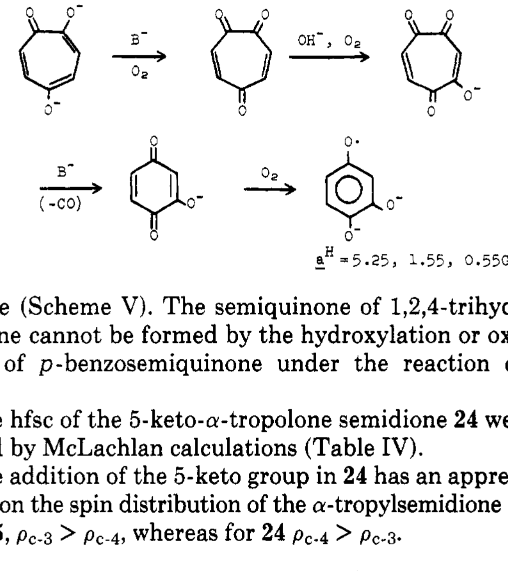
spin density	$n = 1.8, k = 1.4$	$h = 2.0, k = 1.4$
C_3, C_7	0.0464	0.0407
C_4, C_6	0.0797	0.0826

[a] $\alpha_O = \alpha + h\beta$; $\beta_{CO} = k\beta$, $\lambda = 1.2$.

Scheme IV

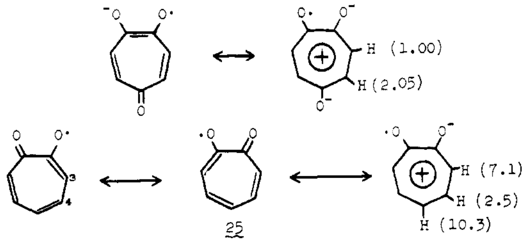


Scheme V



The hfsc of the 5-keto-α-tropolone semidione **24** were assigned by McLachlan calculations (Table IV).

The addition of the 5-keto group in **24** has an appreciable effect on the spin distribution of the α-tropylsemidione (**25**).[14] For **25**, $\rho_{C\text{-}3} > \rho_{C\text{-}4}$, whereas for **24** $\rho_{C\text{-}4} > \rho_{C\text{-}3}$.



Experimental Section

General. The general techniques for the reductions with potassium *tert*-butoxide in dimethyl sulfoxide were followed as previously described.[15] 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 H-cell,[16] 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 solvent 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.

Oxidations in basic solutions were performed by allowing air to enter the H-cell containing the DMSO solution of the dione by separating the ground glass joints of the H-cell and flat cell for brief periods (5–10 s). The solution was then shaken for 1–3 min and its ESR spectrum was then monitored.

Bicyclo[4.2.0]oct-7-ene-2,5-dione. 7,8-Dichlorobicyclo[4.2.0]-octane-2,5-dione monoethylene ketal[2] (12.34 g, 0.0492 mol) was stirred with 19.3 g (0.295 mol) of zinc dust and 6.71 g (0.0492 mol) of zinc chloride in refluxing 95% ethanol for 6 h. Filtration, hydrolysis, ether extraction, and evaporation yielded a material which was chromatographed on a silica gel column with ethyl acetate (15%)–chloroform (85%) to give 5.82 g (0.0323 mol) of the monoethylene ketal of bicyclo[4.2.0]oct-7-ene-2,5-dione, bp 104 °C (0.6 Torr), in 66% yield: IR ($CHCl_3$) 1709, 1452, 1412, 1369, 1322, 1118 cm^{-1}; NMR ($CDCl_3$) δ 1.43–2.70 (m with d at 2.48, 4 H), 3.05–3.30 (m, 1 H), 3.43–3.56 (m, 1 H), 4.03 (s, 4 H), 6.10 (m, 1 H), 6.32 (m, 1 H); MS *m/e* 180 (M^+, 56), 99 (100), 66 (63).

Anal. Calcd for $C_{10}H_{12}O_3$: C, 66.73; H, 6.71. Found C, 66.49; H, 6.67.

Hydrolysis of the monoethylene ketal of bicyclo[4.2.0]oct-7-ene-2,5-dione was difficult. A solution of 0.50 g (2.78 mmol) in 5 mL of dioxane containing 3 mL of 3% sulfuric acid was stirred under nitrogen for 24 h at 25 °C. The solution was neutralized with aqueous sodium bicarbonate, saturated with sodium chloride, and continuously extracted with ether for 48 h to give, after drying and evaporation of the ether, 0.35 g of product contaminated with the starting ketal. Chromatography on silica gel [ethyl acetate (20%)–benzene (80%)] gave 0.090 g (0.66 mmol, 4%) of the dione and 0.21 g of recovered ketal. The dione was a light-yellow oil with appreciable water solubility: IR (film) 1712, 1310, 1270, 1178, 819, 762, 685 cm^{-1}; NMR ($CDCl_3$) δ 2.46–3.33 (m, 4 H), 3.82 (s, 2 H), 6.36 (s, 2 H); MS *m/e* 136 (M^+, 36), 108 (42), 93 (27), 79 (100), 63 (86).

High-resolution mass spectrum: Calcd for $C_8H_8O_2$, 136.05242. Found 136.05236.

The dione was also prepared by reduction of bicyclo[4.2.0]octa-3,7-diene-2,5-dione with a 50-mol excess of zinc dust in 10% acetic acid under nitrogen at 90 °C for 1.5 h. After cooling, filtration, and evaporation of the solvent, a crude product was obtained which after chromatography gave a 72% of desired bicyclic enedione.

Bicyclo[4.2.0]octa-3,7-diene-2,5-dione. The dienedione was prepared by the general route of Oda and Kitahari,[17] starting from *trans*-7,8-dibromobicyclo[4.2.0]octa-2,4-diene.[18] Irradiation of the dibromide (14.47 g, 0.0548 mol) of 1 L of acetone for 6 h in Pyrex with a Sylvania DVY 650 W tungsten-halogen projector lamp using hematoporphyrin as a singlet oxygen sensitizer gave 14.79 g (0.05 mol, 91%) of the *trans*-3,4-dibromo-9,10-dioxytricyclo[4.2.2.$0^{2,5}$]deca-7-ene: mp 104–106 °C; NMR ($CDCl_3$) δ 3.57 (m, 2 H), 4.18 (m, 1 H), 4.74 (m, 3 H), 6.73 (ddd, J = 8, 6, 2 Hz), and 7.12 (ddd, J = 8, 6, 2 Hz). Reduction by LAH in THF gave the enediol in 89% yield, mp 129.5–131.0 °C, which was converted to the diacetate with acetic anhydride–pyridine in benzene solution in 94% yield. The diacetate was treated with a fourfold excess of zinc dust and a small crystal of iodine in DMSO at 90 °C to give the crystalline diene diacetate in 90% yield. Reduction of the dienediacetate with LAH in THF gave ~100% of the dienediol which was oxidized to the desired dienedione. A solution of 0.754 g (5.46 mmol) in 100 mL of $CHCl_3$ of the dienediol was treated with 15 g of activated MnO_2[19] for 30 h. Filtration and washing of the filter cake with ethyl acetate followed by evaporation of the solvent gave 0.493 g (3.68 mmol, 67%) of the dione which crystallized as yellow plates: mp 44–46 °C; IR ($CHCl_3$) 1679, 1604, 1560, and 962 cm^{-1}; NMR ($CDCl_3$) δ 3.95 (s, 2 H), 6.37 (s, 2 H), and 6.67 (s, 2 H).

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

2,4-Cyclooctadiene-1,6-dione. The monocyclic dione was prepared by the flash pyrolysis of bicyclo[4.2.0]oct-7-ene-2,5-dione according to the procedure of Oda and Kitahari.[9] Passage of 201 mg (1.48 mmol) of the enedione over silica chips at 500 °C (0.03 Torr) gave 177 mg (1.30 mmol, 88%) of a yellow liquid which was microdistilled at 75 °C (0.1 Torr): NMR ($CDCl_3$) δ 2.84 (2, 4 H), 6.09 (dt, 2 H, J = 12.5, 2.5 Hz), and 6.52 (dt, 2 H, J = 12.5, 2.5 Hz); MS (16 eV) *m/e* 136 (M^+, 30), 108 (100), 94 (94), 80 (28), and 66 (52).

2,5,7-Cyclooctatriene-1,4-dione. The preparation followed the procedure of Oda and Kitahari.[10] The crude pyrolysate of 305 mg (2.24 mmol) of bicyclo[4.2.0]oct-7-ene-2,5-dione was dissolved in 6 mL of CF_3CO_2H (33%)–CH_2Cl_2 (67%) and brominated with 2.20 mmol of NBS for 1 h at 25 °C. The solution was cooled in an ice bath and 4 mL of triethylamine added. Vacuum distillation of the solvent gave a residue which was chromatographed on silica gel [ethyl acetate (5%)–chloroform (95%)] to give 120 mg (0.90 mmol) of crude trienedione. Preparative GLC (0.25 in. × 6 ft DC-550, 150 °C) gave the pure trienedione as a light-yellow solid: IR ($CHCl_3$) 1665, 1616, 1489, 1409, 1128 cm^{-1}; NMR δ 6.03 (dt, 2 H, J = 14, 2 Hz), 6.43 (dt, 2 H, J = 14, 2 Hz), and 6.66 (s, 2 H); MS *m/e* 134 (M^+, 22), 106 (18), 78 (100), 52 (64).

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

5-Hydroxytropolone. Following the procedure of Oda and Kitahari,[20] tropone was photooxidized with singlet oxygen using hematoporphyrin in acetone as the sensitizer to yield 56% of the endoperoxide. The endoperoxide (2.76 g, 0.02 mol) in 50 mL of 95% ethanol was stirred at 0 °C and 2.22 g (0.022 mol) of triethylamine in 100 mL of 95% ethanol was added over a period of 2 h.[21] The product was evaporated under vacuum, and the residue was washed with ethanol and sublimed to yield 5-hydroxytropolone: mp 246–247 °C [lit.[22] 245 (dec)]; NMR (DMSO-d_6) δ 6.95 (m, 4 H), 9.3 (m, 2 H).

1,6,7,8-Tetramethyl-3,4-benzobicyclo[4.2.0]octa-3,7-diene-2,5-dione (6d). 2,3-Dimethylnaphthoquinone (0.01 mol) and 2-butyne (0.04 mol) in 250 mL of benzene were irradiated in Vycor with a 275-W sunlamp for 70 h under nitrogen. The solvent was evaporated, and the resulting red oil was dissolved in ether and shaken with a 10% solution of sodium dithionite in 1 N NaOH to remove unreacted quinone. Evaporation of the solvent and recrystallization from CCl_4 gave 5.5% of **6d**: mp 135–136.5 °C (lit.[23] 139–140 °C); ^1H NMR ($CDCl_3$) δ 1.47 (s, 6 H), 1.51 (s, 6 H), and 7.16–8.19 (m, 4 H).

1,6-Dimethyl-8-phenyl-3,4-benzobicyclo[4.2.0]octa-3,7-diene-2,5-dione (6c). 2,3-Dimethylnaphthoquinone (0.013 mol) and phenylacetylene (0.019 mol) in 250 mL of benzene were irradiated in Vycor for 10 h under nitrogen. The unreacted quinone was removed with NaOH–sodium dithionite to give 36% of **6c** after recrystallization from ethanol: mp 140.0–140.7 °C (lit.[23] 140–141 °C); ^1H NMR ($CDCl_3$) δ 1.64 (s, 3 H), 1.78 (s, 3 H) and 6.53 (s, 1 H), 7.23–7.59 (m, 5 H), and 7.65–8.30 (m, 4 H).

Other Reagents. The synthesis of the 7,8-dimethyl-3,4-benzobicyclo[4.2.0]octa-3,7-diene-2,5-dione **(6b)** has been previously described.[2] Compounds **6a, 6c, 6f, 16a,** and **16b** were kindly supplied by Professor S. D. Pappas.[24]

Registry No.—1 (R = H), 54338-59-9; 1 (R = CH_3), 66562-80-9; **3a,** 54338-83-9; **3a** 7,8-dichloromonoethylene ketal, 66562-81-0; **3a** monoethylene ketal, 66562-82-1; **3b,** 66562-73-0; **4a,** 54338-66-8; **4b,** 54338-67-9; **11,** 56614-08-5; **12,** 66562-69-4; **13,** 66562-70-7; **14a,** 54338-63-5; **14b,** 54338-64-6; **14c,** 54338-65-7; **15b,** 66609-87-8; **15f,** 54338-89-5; **19,** 66562-71-8; **23,** 66562-72-9; **24,** 56746-06-6; **25,** 53875-14-2; *trans*-7,8-dibromobicyclo[4.2.0]octa-2,4-diene, 27587-70-8; *trans*-3,4-dibromo-9,10-dioxytricyclo[4.2.2.$0^{2,5}$]deca-7-ene, 66562-74-1; tropone, 539-80-0; 5-hydroxytropolone, 15852-34-3; 2,3-dimethylnaphthoquinone, 2197-57-1; 2-butyne, 503-17-3; phenylacetylene, 536-74-3.

References and Notes

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Generality of the Photochemical Bicycle Rearrangement. Exploratory and Mechanistic Organic Photochemistry[1,2]

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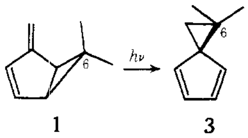
The generality of the slither, or bicycle, rearrangement has been examined in three new systems: 2-methylene-4,6-diphenylbicyclo[3.1.0]hex-3-ene (**5**), 3,4-benzo-2-methylene-6-phenylbicyclo[3.1.0]hex-3-ene (**6**), and 3,4-benzo-6-(4-methoxyphenyl)-2-methylenebicyclo[3.1.0]hex-3-ene (**7**). In each case endo and exo stereoisomers were studied. The photochemistry of these systems consisted of slither rearrangements in which carbon-6, with its two sp^5 three-ring orbitals, bicycles around the five-ring and also out onto the exocyclic methylene group. The stereospecific slithering process is termed "bicycling", since C-6 moves stereospecifically around the five-ring with the sp^5 orbitals acting as "wheels". With the wheels staying on the five-ring and exocyclic bonds, the endo group remains endo and the exo group at C-6 remains exo. Counterclockwise bicycling is shown to be preferred to clockwise bicycling (with the molecule drawn following the convention in the text). Evidence is presented in the case of diphenyl bicyclic olefin for a minor pathway permitted for the endo but not exo stereoisomer. This involves counterclockwise bicycling just past the *exo*-methylene group followed by backup onto this exo moiety to give the stereoisomer of the major spiro product. In the benzo examples, bicycling over the π system of the benzo moieties is shown to be inhibited. SCF–CI calculations were carried out for the reacting species along the excited state surface leading toward product. This surface curves downward until a cyclopropyl diradical structure is reached, at which point an approach to the ground-state surface is encountered. Correlation diagram treatments were derived as well. Finally, a concept of dissection of electronic excitation into components around the molecule was introduced. This involved a $\Delta\mathbf{P}$ matrix giving the change in bond orders of the excited state vs. the ground state. The treatment allows one to determine which molecular motions lead to a mutual approach of excited and ground states and predicts reaction pathways.

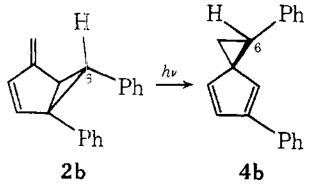
Introduction

Previously we have described the photochemical rearrangement of 6,6-dimethyl- and 5,6-diphenyl-substituted 2-methylenebicyclo[3.1.0]hex-3-enes (**1** and **2**, respectively) to give spiro[2.4]hepta-4,6-diene products (**3** and **4**).[3] The reaction was shown to proceed via the excited singlet and to be stereospecific in the one case with stereochemistry (note eq 1).



(1a)

1 3



(1b)

2b 4b

The reaction is one in which carbon-6 slithers, or bicycles, along the surface of a fulvene π system, retaining stereochemistry in such a way that the endo group at C-6 remains endo and the exo group remains exo. The reaction stereochemistry can be envisaged as involving two sp^5 hybrid orbitals bonding C-6 to the five-ring, these orbitals constituting "bicycle wheels". As the forward wheel rolls along the five-ring, the inside (endo) handlebar remains inside the five-ring and the exo one remains outside.

Because of the intriguing nature of this new reaction, we wished to explore its generality, its limitations, and structural effects governing the reaction course. Also, our single photon counting technique for determining excited singlet rate constants[4] provided a way to ascertain the reaction facility as a function of structure.

The systems selected for study were 2-methylene-4,6-diphenylbicyclo[3.1.0]hex-3-ene (**5**), 3,4-benzo-2-methylene-6-phenylbicyclo[3.1.0]hex-3-ene (**6**), and 3,4-benzo-6-(4-methoxyphenyl)-2-methylenebicyclo[3.1.0]hex-3-ene (**7**). These promised to provide information on the generality of the reaction as a function of structure and also indicate if the reaction still occurred with benzo substitution. Additionally, the compounds were selected so that fluorescence emission could be used to monitor excited-state decay.

Synthesis of Reactants and Potential Photoproducts. The synthesis of the exo and endo isomers of diphenyl diene **5** (i.e., **5a** and **5b**)are shown in Scheme I; synthesis of the exo and endo isomers of benzo phenyl bicyclic olefins **6a** and **6b** and the corresponding anisyl analogues **18a** and **18b** are shown in Scheme II.

One novel feature of our synthetic efforts is the intramolecular cyclization of the α,β:γ,δ-unsaturated diazoketones (e.g., **10a,b**). Another is the three-ring formation by reaction of dimethylsulfoxonium methylide with methyleneindene π bonds to form **20a** and **22a** (note Scheme III).

With the photochemical reactants in hand, it proved stra-

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