

where a denotes activity and f is an activity coefficient. Let us now consider the free energy of transfer of A^- ($\Delta G_{T,A^-}$) from one solvent to another and follow Hepler³¹ in expressing the free energy in terms of the external and internal enthalpy and entropy, *i.e.*

$$\Delta G_{A^-} = \Delta H_{E,A^-} + \Delta H_{I,A^-} - T\Delta S_{E,A^-} - T\Delta S_{I,A^-} \quad (2)$$

The internal enthalpy and entropy will be independent of the solvent and the external quantities can be related by the isokinetic relationship ($\Delta H_E = \beta\Delta S_E$).³¹ Thus the free energy of transfer of A^- becomes

$$\Delta G_{T,A^-} = RT \ln \frac{f_{A^-}'}{f_{A^-}} = \Delta H_{E,A^-}(1 - T/\beta) \quad (3)$$

The change in the acidity function as the solvent is changed is given by

$$\delta H_- = \log \frac{a_{H^+}' f_{AH}'}{a_{H^+} f_{AH}} + \log \frac{f_{A^-}'}{f_{A^-}} \quad (4)$$

Combining eq 3 and 4 gives

$$\delta H_- = \log \frac{a_{H^+}' f_{AH}'}{a_{H^+} f_{AH}} + \frac{\Delta H_{E,A^-}}{2.3RT}(1 - T/\beta) \quad (5)$$

The heat of transfer of sodium methoxide can be expressed as $\Delta H_{T,NaOMe} = \Delta H_{T,Na^+} + \Delta H_{T,-OMe}$. Com-

(31) L. G. Hepler, *J. Amer. Chem. Soc.*, **85**, 3089 (1963), and references cited therein.

binning this with eq 5 and remembering that

$$\frac{\Delta H_{T,Na^+}}{RT}(1 - T/\beta) = - \ln \frac{a_{Na^+}'}{a_{Na^+}}$$

gives

$$\delta H_- = \log \frac{a_{H^+}' a_{Na^+}' f_{MeOH}}{a_{H^+} a_{Na^+}' f_{MeOH}'} + \frac{\Delta H_{T,NaOMe}}{2.3RT}(1 - T/\beta) \quad (6)$$

Thus, if the activity coefficient term in eq 6 is a constant a straight line plot of H_- vs. $\Delta H_{T,NaOMe}$ is expected. If the activity coefficient ratio f_{MeOH}/f_{MeOH}' is constant, or nearly so (a rather unlikely occurrence), the observed behavior requires that the activities of H^+ and Na^+ be affected in the same way by changes in the solvent composition. This is surprising, since significant differences even in the solvation of Li^+ and Na^+ in DMSO have been observed.³² It does not seem reasonable to expect the activity coefficient term would be a constant and this relationship is being explored further.

Acknowledgment. Partial support of this work through grants made by the Research Corporation and the National Science Foundation (to J. W. L.) as well as by the Atomic Energy Commission (to J. H. F.) is gratefully acknowledged

(32) B. W. Maxey and A. I. Popov, *ibid.*, **91**, 20 (1969).

Heterocyclic Radical Ions. V. Electron Spin Resonance Splittings of Semifuraquinones¹

Stephen F. Nelsen,*² Enrique F. Travecedo,³ and Errol D. Seppanen

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. Received January 22, 1970

Abstract: The esr spectra of several rigid, strained dialkylmaleic anhydride anions (semifuraquinones) are reported and discussed. These were prepared by reduction of Diels–Alder adducts of dichloromaleic anhydride and cyclic dienes. The polarography of several of the adducts and related compounds was investigated, and it was concluded that both C–Cl bonds are being broken in the slow step of the reduction. The adducts of cyclopentadiene and dimethylfulvene with dibromomaleic anhydride were also prepared and reduced, and esr spectra of the semifuraquinones are reported.

Long-range proton esr splitting constants are especially large in rigid, strained systems, and the factors leading to the enhanced odd-electron delocalization in such situations have been a subject of interest for about 5 years. To study such splittings, some group which can be converted to a conveniently stable radical is needed to “spin label” the aliphatic portion of the molecule of interest. Semidione spin labels have been extensively employed by Russell’s group,⁴ and semifuraquinones by Stock’s group.⁵ We have chosen

the dialkylmaleic anhydride anion (“semifuraquinone” group) for similar studies.¹ Semifuraquinone is a very similar spin label to semiquinone in that the signs of the p orbitals in position to overlap with the aliphatic portion of the molecule (the C_α p orbitals) are opposite, but have a higher spin density in the semifuraquinone; since resolution is a major problem in these experiments, the greater expected splitting constants and the lack of splittings introduced by the label are valuable assets of semifuraquinones. Semidione is fundamentally different from the quinone-type spin labels, for the signs of the C_α p orbitals are the same; the π spin density at the C_α carbons is also somewhat higher for semidione than for semifuraquinone. The semifuraquinone spin label was also attractive to us because it is easy to introduce by Diels–Alder reactions of acetylenedicarboxylic acid

(1) Preliminary report: S. F. Nelsen and E. D. Seppanen, *J. Amer. Chem. Soc.*, **89**, 5740 (1967).

(2) Alfred P. Sloan Fellow, 1968–1970.

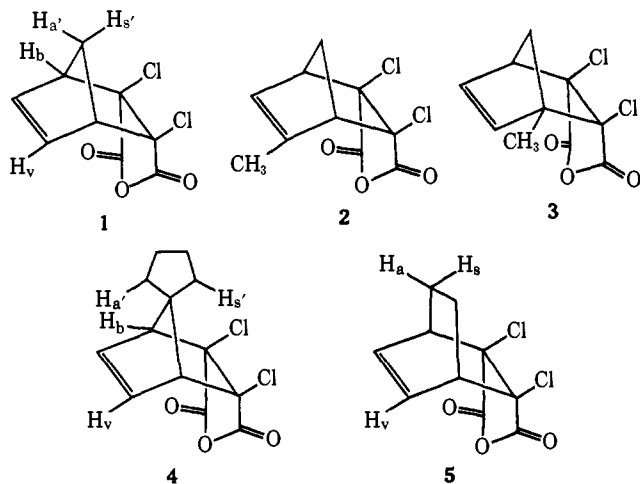
(3) Ford Foundation Fellow.

(4) G. A. Russell, G. W. Holland, and K. Y. Chang, *ibid.*, **89**, 6629 (1967), and references therein.

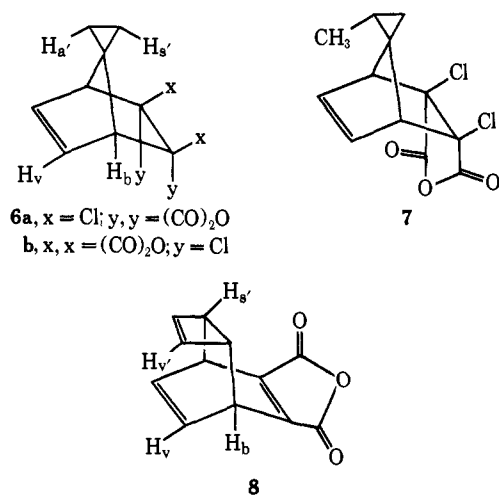
(5) D. Kosman and L. M. Stock, *ibid.*, **91**, 2011 (1969), and references therein.

derivatives⁶ or dihalomaleic anhydride derivatives. Although it is difficult to convert many dihalomaleic anhydride adducts to maleic anhydride derivatives because of over reduction,⁷ this proves to be unnecessary for esr work, since *intra muros* reduction in the esr cavity forms semifuraquinones without any detectable radical intermediates.

Diels-Alder Adducts of Dichloromaleic Anhydride. The adducts we used as precursors for the rigid bicyclic semifuraquinones were prepared simply by refluxing the components in toluene or xylene. For **1-5** no evidence for exo-endo mixtures was observed, and the configuration doubtless is as written, the same as in the maleic anhydride adducts. Methylcyclopentadiene



gave a mixture of **2** and **3**, the former predominating. We obtained pure **2** by fractional crystallization, but never were able to obtain a pure sample of **3**. Confusingly, spiro[4.2]-2,4-heptadiene gave a product which had "twinned" vinyl and bridgehead nmr absorption (and a complex cyclopropyl pattern), which we believe to be a 1.5:1 mixture (which we never could separate by crystallization, sublimation, or tlc) of endo and exo adducts (**6a** and **6b**). The 6-methyl derivative only gave a



single compound (by nmr), which we formulate as the *anti*-methyl **7** on steric grounds, but only write as endo for convenience.

(6) Dialkylmaleic ester derivatives are generally less suitable than the anhydrides because of stability and line width problems. See S. F. Nelsen and E. F. Travedo, *Tetrahedron Lett.*, 2685 (1969).

(7) H. D. Scharf and F. Korte, *Chem. Ber.*, **98**, 764 (1965).

Table I. Splitting Constants for Some Bicyclic 5,6-Unsaturated Semifuraquinones

Radical anion	Splitting (no. H)	Assignment
1A	1.41 (1)	H _a '
	0.79 (3)	H _v and H _s '
	0.40 (2)	H _b
4A	Ca. 0.77 (4)	H _a ' and H _v
	Ca. 0.42 (4)	H _s and H _b
5A	1.55 (2)	H _a
	1.18 (2)	H _v
	0.33 (2)	H _s
6A	1.07 (2)	H _a '
	0.81 (2)	H _v
	0.52 (2)	H _s and H _b
	0.46 (2)	H _b
7A	0.98 (1)	H _a '
	0.82 (2)	H _v
	Ca. 0.49 (4)	H _s ' and H _b
8A	0.91 (2)	H _v
	0.35 (4)	H _v ', H _a
	0.10 (2)	H _b

The observed splitting constants for the dechlorinated radical anions appear in Table I. Assignments are consistent with earlier work.⁴⁻⁵ **8A** was generated from **8**, a previously reported compound.⁸ Unfortunately, we have been unable to obtain sufficient resolution to extract the splitting constants from the esr spectrum of **2A** (with 128 lines in under 5 G this is not surprising), but it is 4.06 G wide, or about the same width as **1A**. From the width and complexity of the spectrum we believe that the methyl splitting may be 30-50% the size of the vinyl proton splitting.

We also prepared semifuraquinones from hydrogenated **1**, **5**, **6**, and **7**; the splitting constants appear in Table II.

Table II. Splitting Constants of Saturated Bicyclic Semifuraquinones

Radical anion	No.	Splitting (no. H)	Assignment
	9A	2.34 (2)	H _a
		1.03 (1)	H _a '
		0.47 (1)	H _s '
		0.37 (2)	H _s and H _b
		0.27 (2)	H _s and H _b
	10A	2.09 (2)	H _a
		0.46 (4)	H _a ' and H _b (?)
		0.23 (4)	H _s and H _s '(?)

	11A	2.11 (2)	H _a
		0.46 (3)	H _a ' and H _b (?)
		0.23 (4)	H _s and H _s '(?)

	12A	1.36 (4)	H _a
		0.27 (4) ^a	H _s

^a Our earlier report¹ of **2** was in error.

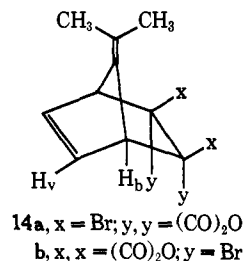
We have been completely unsuccessful in attempts to observe semifuraquinones from 1,2 adducts of dihalomaleic anhydrides and imides with olefins;⁹ this was

(8) W. Reppe, *et al.*, *Justus Liebigs Ann. Chem.*, **560**, 1 (1948).

(9) We thank Professor H. Dieter-Scharf for generous supplies of these compounds.

probably caused by the very negative reduction potentials of these compounds (see below).

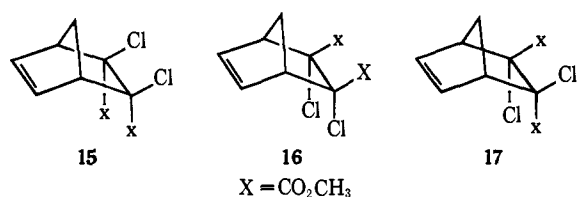
Dibromomaleic anhydride adducts were examined as precursors for semifuraquinones, but were found to be less convenient both to prepare and to reduce to semifuraquinones. The cyclopentadiene adduct (**13**) did give the esr spectrum of **1A** identical with that generated from the dichloromaleic anhydride adduct or the unsaturated anhydride. We did use the dibromomaleic anhydride adduct with 6,6-dimethylfulvene, because dichloromaleic anhydride rapidly polymerized this compound in several attempts at preparation of a Diels–Alder adduct. At room temperature in ether, a moderate yield of a mixture of 1:1 adducts was obtained (**14a**, **14b**), as shown by nmr and mass spectra. One isomer could



easily be obtained pure by crystallization, but the minor adduct was not successfully purified. We were unsuccessful in attempts to debrominate these compounds with iodide ion or zinc. Reduction of the pure isomer of **14** to the semifuraquinone was most successful using tetrabutylammonium iodide as supporting electrolyte, but this species was frustratingly unstable. The esr spectrum observed consisted of at least 23 lines in three major groups covering 3.03 G, and was consistent with a (2 H) = 0.96 (H_v), a (6 H) = 0.28 (H_{Me}), a (2 H) = 0.14 (H_b). 5,6-Dihydro-**14** was prepared, and its semifuraquinone showed the *ca.* 2-G triplet expected for the H_a splitting, but the complexity of the small splitting pattern was so great we were unable to analyze it—clearly the methyl hydrogens were splitting significantly here, also.

The cyclopentadiene–chloranil adduct¹⁰ was reduced, giving the esr spectrum of 2',3'-dichloro-**1B**, which showed splittings of 0.8 (1 H) and 0.4 (3 H), making the spectrum virtually identical with that of **1B** but lacking the quinone splittings. The line widths were greater than for **1B**, however, which showed that the dichloro-semiquinone spin label is unattractive for esr work.

For polarographic studies, we prepared the three possible 2,3-dichloro-2,3-biscarbomethoxy-5-norbornenes. Only one of the *cis*-dichloro diesters (**15**) was obtained from acid-catalyzed methanolysis of **1**, but a 3:1 mixture of **15** and **16** resulted from Diels–Alder addition of cyclopentadiene and dimethyl dichloromaleate, and **17** was the sole product using dimethyl dichlorofumarate.



(10) W. Albrecht, *Justus Liebigs Ann. Chem.*, **348**, 45 (1906).

Discussion of ESR Splitting Constants

Our best evidence for the spin density at C_α in semifuraquinones relative to semiquinones and semidiones comes from the 6.10-G methyl splitting of dimethylmaleic anhydride.¹¹ The corresponding semiquinone has a methyl splitting of 1.71 G,¹² and the *cis*-semidione has a 7.0-G splitting.¹³ Using a value of Q_{βCH₃} of 27, the spin densities at C_α for the three spin labels are about 0.22, 0.06, and 0.26. The spin density ratio of semifuraquinone to semiquinone in bicyclic compounds does not appear to be as high as that predicted here, however, and observed splitting constant ratios for rigid compounds fall in the range 2–3.

The homoconjugated vinyl splittings of Table I have been discussed elsewhere.^{1,11} We only wish to point out here that interpretation of the reason for the large increase of α_v in going from cyclohexadienyl to bicyclic systems is very complicated, and that spin polarization seems to be an important mechanism. Our failure to be able to evaluate the methyl splitting for **2A** is less important than it originally seemed in the light of our studies in cyclohexadienyl systems.¹¹ Because of the symmetry of the highest occupied MO of the semifuraquinone label, the H_a'–C₇–H_s' group of **1A** and **9A** lies directly in a nodal plane, and contributions to these γ splittings arising from “homohyperconjugation” and “C₆–C₇ hyperconjugation”⁴ should be entirely cancelled. By such cancelling the 6.54-G H_a' splitting of **9C** is reduced to 1.05 G in **9A** (*vs.* 5.73 G expected just from the A/C spin density ratio); such hyperconjugative mechanisms seem quite important in generating the very large “W plan” γ splittings seen in semidiones. No such cancellation effect is seen in the H_s' splitting, making it unlikely that C–C hyperconjugation is of great importance in generating the small H_s' splitting, and therefore also for the large H_a' splittings. In **4A**, **6A**, **7A**, **10A**, and **11A**, H_a' and H_s' are replaced by carbon atoms of a spiro ring, yet hydrogens attached to these carbons still show significant splittings. The H_a' splitting ratio of **4A/1A** is 0.54, significantly larger than the 0.081 ratio for 7-*anti*-methyl substitution on 1-C.¹⁴ This would be qualitatively understandable if the spin were transmitted to the 7-*anti* position partially by interaction of antisymmetric combination of the C₇ orbitals with the antisymmetric semifuraquinone MO, because the H_a' hydrogens of **4A** would then be held close to the most favorable position for overlap and one would expect an enhancement in splitting constant over that for a freely rotating methyl group.^{15a} The methyl label on **7A** and **11A** demonstrates that it is still the anti splitting that is largest in these spiro compounds, although both syn and anti C–C bonds are still in the nodal plane. Increasing the strain in the spiro ring by contracting it from five to three carbons atoms increases the H_a' splitting by 39%; increased strain has often been observed to increase splittings.^{4,5} It is interesting that saturating the double bonds of **6A** and **7A** decreases the H_a' split-

(11) S. F. Nelsen and E. D. Seppanen, *J. Amer. Chem. Soc.*, **92**, 6212 (1970).

(12) B. B. Venkatraman, B. G. Segal, and G. K. Fraenkel, *J. Chem. Phys.*, **30**, 1066 (1959).

(13) G. A. Russell, S. T. Stone, E. R. Talatay, and S. A. Weiner, *J. Amer. Chem. Soc.*, **88**, 1998 (1966).

(14) G. A. Russell and K. Y. Chang, *ibid.*, **87**, 4381 (1965).

(15) (a) This was first suggested to us by Professor Leon M. Stock; (b) T. M. McKinney, *J. Amer. Chem. Soc.*, **90**, 3879 (1968).

ting by a factor of 2; perhaps the vinyl π system is also included in the obviously very complicated mechanisms involved in long-range spin delocalization. Our spectrum of **8A** closely parallels that reported by Kosman and Stock for **8B**,⁵ except for our observation of a tiny bridgehead splitting. A bridgehead splitting in a [2.2.2]octyl system has previously been observed in the dibenzodicyano case.^{15b}

The bridgehead splitting of **9A** (whether it is 0.27 or 0.37 G) shows an even larger cancellation effect compared to **9C** (2.43 G) than the H_a' splitting, and it seems unreasonable to attribute this solely to an effect of cancellation of C_6-C_7 hyperconjugation since the H_s' splitting showed little effect. One possibility would be an interaction of the C_6-H_6 bond with a combination of C_7 orbitals including the C_7-H_a' orbital, which bears considerably more spin in the semidione than the semifuraquinone case. In furan adducts, where the $H_a'-C_7-H_s'$ orbitals are replaced by lone pairs on oxygen, the bridgehead splittings are substantially larger in a case with the symmetry of semifuraquinone.¹⁶ Crossing interactions and geometrical differences can, of course, also contribute to the observed cancelling on going from semifuraquinone to semidione.

For the aliphatic splittings which do not have cancelled hyperconjugative contributions (labeled H_a in the drawings), the semidione to semifuraquinone splitting ratios are 1.19 (**9**), 1.53 (**12**), and 1.67 (**5**), and the H_s ratio for **12** is 1.25 (to be compared with 1.14 expected from the splittings of the dimethyl compounds). This sort of agreement is probably no worse than expected in view of the slight geometrical differences and experimental uncertainty in the splittings.

The isopropylidene double bond of **14a** is also held rigidly in the nodal plane of the semifuraquinone group, yet the methyl hydrogens (formally ϵ to the spin-bearing p orbitals) still show a splitting of about 0.28 G. In view of the uncertainties about expected splittings of vinyl methyl groups,¹¹ we can draw no conclusions about the mechanism of spin delocalization here.

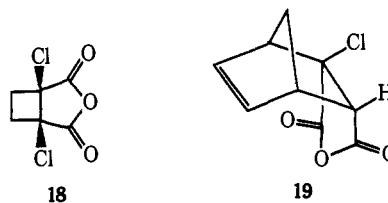
Polarography of Dichloromaleic Anhydride Adducts. Polarograms of a number of the compounds from which esr spectra were observed have been determined under conditions similar to those of the esr experiments. 3-Methyl-, 3,6-dimethyl-, and 4-methyl-3,6-dihydrophthalic anhydride each gave a wave at -1.06 to -1.08 V (*vs. sce*) with an observed slope of $0.055-0.06$ V, as expected for a reversible one-electron reduction to the semifuraquinone. 2-Norbornene-2,3-dicarboxylic anhydride reduced slightly more easily ($E_{1/2} -0.99$, slope 0.067). Dichloromaleic anhydride itself gave waves with $E_{1/2}$ values of -1.07 (slope 0.19) and -1.42 (slope 0.05). Its adducts with dienes reduced surprisingly easily, the results being summarized in Table III. Compounds **11** and **7** showed a maximum at the top of the first wave, followed by and overlapping with another, lower wave; this made it impossible to determine the $E_{1/2}$ and slopes very accurately. The slopes quoted in Table III are for the lower portion of the first wave; the slope increased near the maximum. The position of the second wave for these compounds is consistent with the interpretation that the two chlorines are reduced off at the first wave, followed by reduction of

Table III. Polarographic Data for Dichloromaleic Anhydride Diels-Alder Adducts

Compd	$E_{1/2}^a$	Slope ^b	$i_D, \mu A/mmole$
5	$-0.69 (-1.03)^c$	0.14 ^c	3.8 (2.5) ^c
1	$-0.88 (-1.05)^c$	0.13 ^c	3.9 (0.8) ^c
4	-0.91	0.15	4.1
6	-1.11	0.23	4.8
7	-1.09	0.20	4.3
18	-1.7	0.38	5.7
19	-1.4	<i>d</i>	2.8

^a *vs. sce*. ^b From a V *vs.* $\log(i/(i_D - i))$ plot. ^c A maximum separates the waves, see text. ^d Very broad, extending from ca. -1.15 to -1.65 , with a break to lower slope near -1.4 .

the resulting dialkylmaleic anhydride to semifuraquinone at the second wave. The 7,7-dialkylbicyclo[2.2.1]heptane systems **4**, **6**, and **7** only gave one wave, presumably because the chloride reductions occurred in the same region as that for reduction of the dialkylmaleic anhydride. The cyclobutane system **18** gave an



extremely broad wave centered over 1 V more cathodic than the related bicyclo[2.2.2]octane systems. The monochloro anhydride **19** also reduced at a more cathodic potential than the dichloro anhydrides (except **18**) and gave a broad wave. We also determined polarograms of the three dichloro diesters in the bicyclo[2.2.1]heptane series (**15-17**). All three were much more difficult to reduce than the anhydrides and gave broad waves starting about -1.47 and centered at -1.6 to -1.8 V; **16** and **17** also gave maxima near -1.8 .

The polarography of several vicinal dibromohydrocarbons was studied by Závada, Krupička, and Sicher,¹⁷ who found substantial dependence of $E_{1/2}$ on structure. A Karplus-type curve was observed in a correlation of reduction potential with the torsion angle between the two C-Br bonds in rigid structures; alkyl monobromides seemed to fit the curve well for a 90° point. Recently Rifi¹⁸ has presented both polarographic and product study evidence for the reduction of 1,3-dibromopropane and triethyl-3-bromopropylammonium bromide being concerted.

Our studies indicate that to observe the low reduction potentials of the upper entries in Table III, it is necessary not only to have a vicinal dichloride, but also to have proper alignment of the carbonyl groups. The effect of alignment of carbonyl groups is seen in more attenuated form in cyclic α -halo ketones, where the axial compounds reduce less cathodically than the equatorial ones.¹⁹ Yet increased ring strain clearly makes the reduction of our compounds much more difficult. These results seem consistent with the possibility of a concerted, two-electron reduction with double chloride expulsion being the slow step in the reduction of the upper entries of Table III. It seems to us difficult to explain

(17) J. Závada, J. Krupička, and J. Sicher, *Collect. Czech. Chem. Commun.*, **28**, 1664 (1963).

(18) M. R. Rifi, *Tetrahedron Lett.*, 1043 (1969).

(19) A. M. Wilson and N. C. Allinger, *J. Amer. Chem. Soc.*, **83**, 1999 (1961).

(16) S. F. Nelsen and E. F. Travecedo, *Tetrahedron Lett.*, 2685 (1969).

the large changes in reduction potential for the other compounds run without having a significant degree of breaking for both C-Cl bonds in the transition state leading to reduction.

Experimental Section

Materials. The spirocyclopentadienes were prepared by known methods.²⁰ From 1,2-dibromopropane and sodium cyclopentadienide in liquid ammonia we obtained 6-methylspiro[4.2]hepta-2,4-diene, bp 56–59° (40 mm), in 54% yield, nmr (CCl₄) δ 6.5–5.83 (m), 1.2–2.2 (m) in 3:2 ratio.

Dichloromaleic anhydride adducts were prepared by refluxing equimolar amounts of diene and anhydride 6–12 hr in toluene or xylene—longer reflux times lead to lower yields. After removal of solvent *in vacuo*, the residue was sublimed at 80–120° (0.2 mm) and the sublimate crystallized from Skelly B. Melting points and nmr data for the adducts appear in Table IV, and analytical data in Table V.

Table IV. Nmr Data for Dichloromaleic Anhydride Diels-Alder Adducts

Compd	Mp, °C	Nmr (δ , CDCl ₃)
1	193–194	6.42 (t, $J_{VB} \sim 1.9$, 2 H _v), 3.54 (a, $J \sim 1.8$, 2 H _b), 2.55 (d of m, $J \sim 10.2$, 1 H _a), 2.25 (d of t, $J_{AB} \sim 1.6$, 1 H _a)
2	106–108	5.91 (m, 1 H _v), 3.27 and 3.29 (2 m, 2 H _b), 2.1–2.65 (AB pattern of m, 1 H _a and 1 H _a), 1.83 (d, $J \sim 1.6$, 3 H)
3		6.05–6.55 (m, 2 H _v), 3.15–3.6 (m, 1 H _b), 2.1–2.65 (AB pattern of m, 1 H _a and 1 H _a), 1.60 (s, 3 H)
4	155–156	6.47 (t, $J \sim 2.1$, 2 H _v), 3.26 (t, $J \sim 2.1$, 2 H _b), 2.2 (m, 2 H), 1.6 (m, 6 H)
5	241–243	5.55 (dd, $J \sim 3.1$, 4.3, 2 H _v), 3.32 (ten line m, 15 sept, 2 H), 2.25 (complex m, 2 H), 1.43 (complex m, 2 H)
6a (major 1:5:1)	131–133	6.63 (t, $J \sim 1.8$, 2 H), 3.90 (t, 2 H _b), complex m at 0.35–1.3
6b (minor)		6.53 (t, $J \sim 2.0$, 2 H _v), 3.01 (t, 2 H _b), major s at 0.73 (4 H)
7	92–94	6.62 (t, $J \sim 1.8$, 2 H _v), 3.23 (q, $J \sim 1.8$, 1 H _b), 3.04 (q, $J \sim 1.8$, 1 H _b), 0.25–1.25 (complex, 6 H; including CH ₃ at 0.97 (s), and mult 0.41, 1 methylene H)
10	178–181	2.25 (quint, 2 H, 2.0) (m, 4 H), 0.7 (m, 4 H)
11	87–88	2.6–1.6 (m, 6 H), 1.05 (m, 5 H), 0.45 (t, $J \sim 2.1$, 1 H)
12	191–194	Broad absorptions 2.5–1.2

endo- and exo-cis-2,3-Dichloro-2,3-bis(carbomethoxy)-5-norbornene (15 and 16). A 5-g sample of dimethyl dichloromaleate and 6.5 g of cyclopentadiene were refluxed in xylene for 12 hr; the solvent was distilled off and the residue fractionated. The fraction boiling at 98–99° (0.15 mm), 0.5 g, was a 3:1 mixture of 16 and 17. The minor isomer (17) was isolated by crystallization from pentane: 90 mg; mp 124–125°; nmr (CDCl₃) δ 6.36 (t, 2 vinyl H), 3.72 (5,6 methoxy H), 3.41 (quint, 2 bridgehead H), 2.50 and 2.34 (2 br lines, 1 H), 1.84 and 1.67 (2 t, 1 H). After two crystallizations of the residue, 130 mg of the main isomer (16) was obtained: mp 65–67°; nmr (CDCl₃) δ 6.20 (t, 2 vinyl H), 3.67 (5,6 methoxy H), 3.20 (quint, 2 bridgehead H), 2.51 and 2.33 (br s, 1 H), 1.88 and 1.72 (2 t, 1 H).

(20) R. Riemschneider, E. Reicholt, and E. B. Grabitz, *Monatsh. Chem.*, **91**, 812 (1960); C. F. Wilcox and R. R. Craig, *J. Amer. Chem. Soc.*, **83**, 3866 (1961).

Table V. Combustion Analyses

Compd		Calcd, %			Found, %		
		C	H	X	C	H	X
2	C ₁₀ H ₈ Cl ₂ O ₃	48.61	3.26	28.70	48.73	3.30	28.63
4	C ₁₃ H ₁₂ Cl ₂ O ₃	54.38	4.21	24.69	54.09	4.08	24.76
5	C ₁₀ H ₈ Cl ₂ O ₃	48.61	3.26	28.70	48.42	3.25	28.77
6	C ₁₁ H ₈ Cl ₂ O ₃	50.99	3.11	27.37	50.82	3.11	27.66
7	C ₁₂ H ₁₀ Cl ₂ O ₃	52.77	3.69	25.96	52.75	3.72	26.12
9	C ₉ H ₆ Cl ₂ O ₃	45.98	3.43	30.16	46.21	3.41	30.05
10	C ₁₁ H ₁₀ Cl ₂ O ₃	50.60	3.86	27.16	50.89	4.02	26.99
11	C ₁₂ H ₁₂ Cl ₂ O ₃	52.38	4.40	25.77	52.52	4.40	25.71
13	C ₉ H ₆ Br ₂ O ₃	33.57	1.88	49.64	33.78	1.91	49.67
14	C ₁₂ H ₁₀ Br ₂ O ₃	39.81	2.78	43.87	39.74	2.83	43.96
15	C ₁₁ H ₁₂ Cl ₂ O ₄	47.33	4.33	25.40	47.18	4.22	25.52
16	C ₁₁ H ₁₂ Cl ₂ O ₄	47.33	4.33	25.40	47.31	4.31	25.63
17	C ₁₁ H ₁₂ Cl ₂ O ₄	47.33	4.33	25.40	47.40	4.29	25.73

There was no cross-contamination to the limits of nmr detection. Refluxing 400 mg of 1 in 10 ml of methanol with 4 drops of concentrated sulfuric acid for 3 hr gave only the material with mp 65–67°.

trans-2,3-Dichloro-2,3-bis(carbomethoxy)-5-norbornene (17) was prepared in a low yield by refluxing the components in xylene for 4 hr and crystallizing the residue from hexane: mp 96–97°; nmr (CCl₄) δ 6.50 (4 br lines, 1 vinyl H), 6.12 (4 br lines, 1 vinyl H), 3.82 (s, 3 methoxy H), 3.75 (s, 3 methoxy H), 3.43 (m, 1 bridgehead H), 3.21 (m, 1 bridgehead H), 2.42 and 2.25 (2 m, 1 H), 1.95 and 1.78 (2 t, 1 H).

2,3-Dibromo-5-norbornadiene-2,3-dicarboxylic anhydride was obtained by refluxing the components 5 hr in benzene and crystallizing the residue from benzene: mp 188–190°; nmr (CDCl₃) δ 6.42 (t, $J \sim 1.5$, 2 vinyl H), 3.63 (quint, 2 bridgehead H), 2.64 (d of m, $J \sim 10.1$, 1 H), 2.22 (d of t, $J_{ab} \sim 1.4$).

Dimethylfulvene-dibromomaleic anhydride adducts were prepared by stirring 7.0 g of anhydride and 3.15 g of 6,6-dimethylfulvene in 75 ml of ether under nitrogen for 24 hr, giving 1.75 g of isomer A, dec pt $\sim 135^\circ$. Partial removal of ether gave 3.2 g of a mixture of isomer A with B, B/A ratio about 0.76 by nmr. We were unable to obtain B pure. Nmr of A showed (CDCl₃) δ 6.54 (t, 2 vinyl H), 4.11 (t, 2 bridgehead H), 1.61 (s, 6 methyl H); mass spectrum (70 eV) parent 360, 362, 364 (*ca.* 2% of base peaks at P – Br, 281, 283. Nmr of B showed (CDCl₃) δ 6.61 (t, 2 vinyl H), 4.11 (t, 2 bridgehead H), 1.74 (s, 6 methyl H).

Cyclopentadiene-chloranil adduct was prepared by the method of Albrecht in 20% yield using overnight irradiation with a GE sunlamp, mp 144–146° (lit.¹⁰ mp 146–146.5°).

Esr Measurements. The radical precursor in *ca.* 1–10 mM concentration in DMSO (distilled from calcium hydride) which was 0.05–0.1 M in tetrabutyl- or tetrethylammonium perchlorate was electrolyzed in the Varian flat cell in the cavity of a Varian E.3 or V-4502 instrument. The calibration of the instrument was periodically checked using semiquinone. All splittings reported are believed to be accurate to ± 0.02 G or 1%, whichever is larger.

Polarographic Measurements. A Sargent 15 polarograph with an ir compensator was employed, and the sce electrodes were isolated from the cell by means of an ungreased stopcock. Reported reduction potentials are not corrected for junction potential.

Acknowledgment. We thank the National Science Foundation, the Research Corporation, and the Wisconsin Alumni Research Foundation for support of this work. We thank Professor L. Stock and Professor D. Evans for helpful discussions and Professor H. Dieter-Scharf for generous supplies of photochemical dihalomaleic anhydride-olefins adducts, Mr. John Gillespie for a sample of 8, and Professor H. W. Whitlock for use of polarographic equipment.