Aliphatic Semidiones. XXVI. 1,4-Semidiones in C_5–C_7 Carbocyclic Systems[1]

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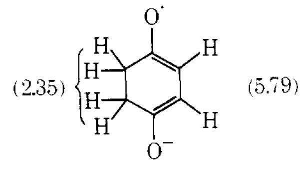
Received June 4, 1974

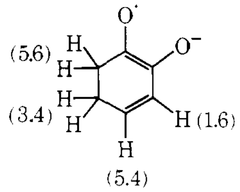
Abstract: Cyclic 1,4-semidiones (radical anions of Δ^2-1,4-diones) have been prepared in the cyclopentane, cyclohexane, and cycloheptane systems and detected by esr spectroscopy. Conformational preference and mobility have been detected in the 1,4-semidiones derived from $\Delta^{8,9}$-1,5-diketohydrindan and $\Delta^{9,10}$-1,6-diketodecalin systems. Examples of valence isomerization are reported in the preparation of 1,4-semidiones from eucarvone, Δ^3-2-acetoxycaren-5-one, 2,3-benzocyclohept-4-enone, and pentacyclo[6.2.2.0^{2,7}.0^{4,10}.0^{5,9}]dodecane-3,6-dione.

1,4-Semidiones (**1**) are more stable[5] than the isomeric conjugated unsaturated 1,2-semidiones (**2**).[6] 1,4-Semidiones have been prepared (a) by the reduction of the 1,4-Δ^2-diones, (b) by oxidation of certain 1,4-saturated diones or (c) of α,β-unsaturated monoketones, or (d) by the condensation reaction of a monoketone and a 1,2-dione in basic solution (Scheme I).



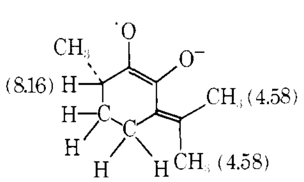
1a

a^H in G



2a[6]

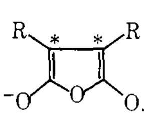
a^H in G, based on composite spectra



2b

$a_{CH_2}{}^H$ = 1.60, 0.90, 0.80, 0.28 G

A variety of 1,4-semidiones involving heterocyclic rings, *e.g.*, **4**,[7,8] **5**,[9] and **6**,[10] are also known.



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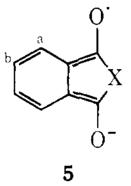
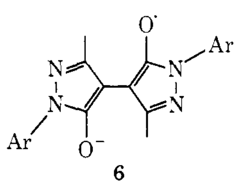


5

X = O, S, NR



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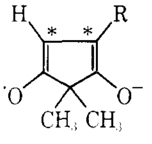
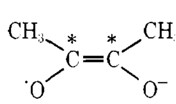


7

a, R = H, a^H = 6.43 (2), a^C = 4.3 (2), 3.00 (1), 1.40 (2), 1.14 (2) G

b, R = CH_3, a^H = 6.5 (3), 5.8 (1)



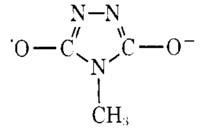
8

$a_{CH_3}{}^H$ = 7.0 G

Electrolytic reduction of 2,2-dimethyl-4-cyclopentene-1,3-dione in DMF, or the reaction of 2,2-dimethylcyclopentane-1,3-dione with a trace of oxygen in the presence of potassium *tert*-butoxide in DMSO, produced semidione **7a** while treatment of 2,2,4-trimethyl-4-cyclopentene-1,3-dione with potassium *tert*-butoxide in DMSO gave **7b**. Semidiones **4**, **7**, and **8** have very similar spin densities at C* as indicated by the values a^H = 6.8 for **4**, R = H;[9] $a_{CH_3}{}^H$ = 6.1 for **4**, R = CH_3;[8] and $a_{CH_3}{}^H$ = 7.0 G for **8**.[11] Spin labels **7** and **8** possess the interesting and valuable property of similar spin density on C* ($-Q_{CH}{}^H \simeq Q_{CCH_3}{}^H$) but different symmetry properties for the MO containing the unpaired electron.[12]

The benzo derivative of **7**, *i.e.*, **5**, X = $C(CH_3)_2$ was prepared by electrolytic reduction of 2,2-dimethylindan-1,3-dione. The spectrum was a triplet of somewhat broad lines, a^H = 2.65 G, which was further resolved by Nelsen[9b] to give a^H = 0.10 (8). The large hfsc is assigned to $a_\beta{}^H$ since the values of a^H are reported to be 0.21 (α) and 2.55 (β) and 0.31 (α) and 2.15 (β) for **5**, X = O and S, respectively.[9a]

The absence of appreciable hfs by the *gem*-dimethyl group in **5** and **7** is consistent with the absence of any delocalization of the electron spin because the methyl groups are in the nodal plane of the spin label.[12,13] This is apparently also the case for the triazolinedione radical anion **9**.



9

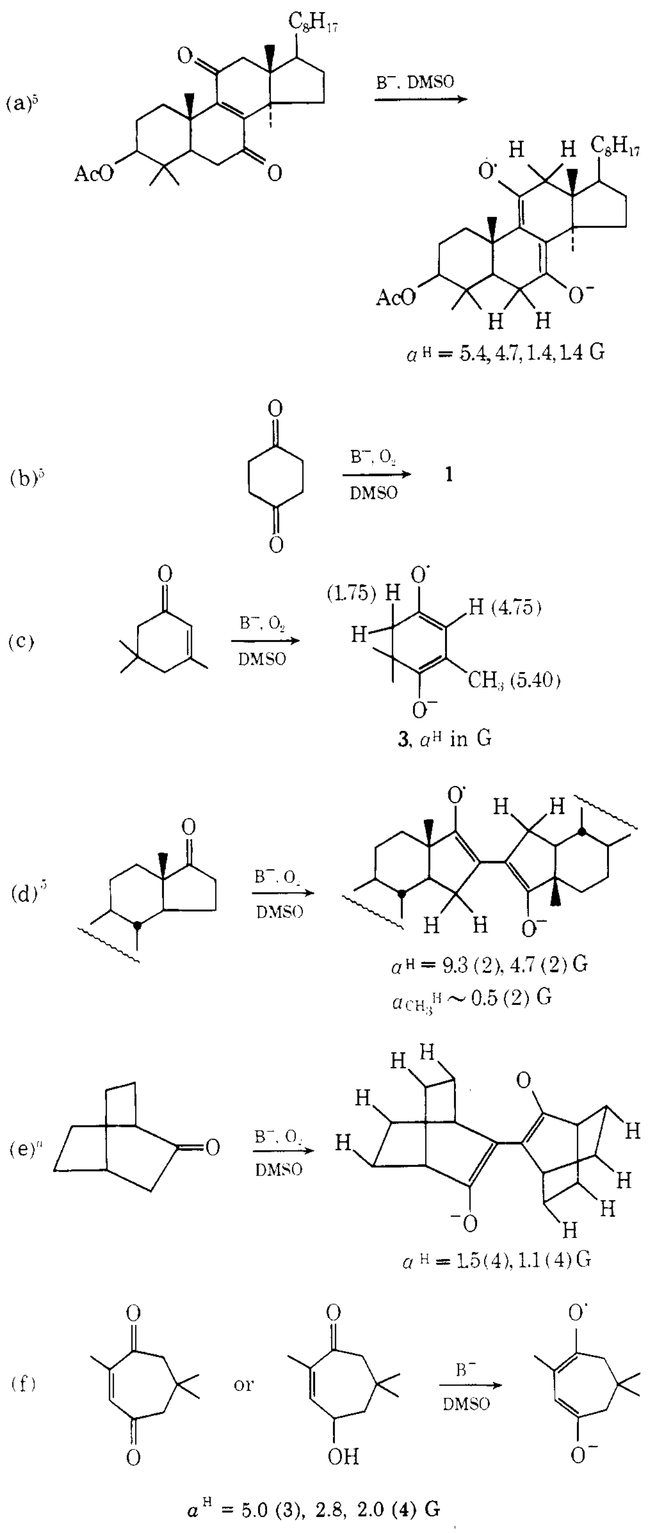
a^N = 4.87, 4.87, 1.85 G

a^H = 0.75 (3) G in DMF

The ^{13}C hfs for **7a** were assigned by synthesis of material enriched with ^{13}C at the methyl group. This clearly showed that $a_{CH_3}{}^C$ = 1.4 G. The other ^{13}C hfs can be assigned as C-1,3 = 1.14, C-2 = 3.00, and C-4,5 = 4.3 G. The hfs for C-2 and the methyl groups of **7a** undoubtedly arises from spin polarization interacting which will be independent of the symmetry of the spin label. Thus, the decrease of a^C from 3.0 G at C-2 to 1.4 G at the methyl groups in **7a** reflects the fall off in spin polarization unaffected by delocalization.

Semidiones **1**, **3**, and **10**,[14] and **11**[15] are considerably more stable than **7** or **5** (X = $C(CH_3)_2$). Semidione **11** is of course easily oxidized to the analogous *p*-benzosemiquinone (a^H = 2.36 (2), 0.80 (1), 0.40 (3) G)[15] as is also observed for the 1,3-cyclohexadiene-*p*-benzoquinone Diels–Alder

Scheme I

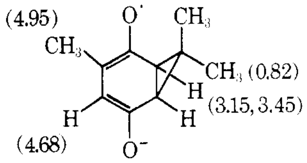


[a] G. A. Russell, G. W. Holland, and K. Y. Chang, *J. Amer. Chem. Soc.*, **89**, 6629 (1967).

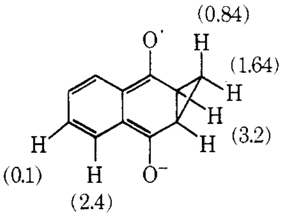
adduct. We have also observed that the pentacyclic dione[16] produces the same semiquinone (Scheme II). This may be a case where by adding an electron to π_{LUMO} a thermally forbidden reaction becomes thermally allowed.[17-19]

As has been reported,[14] **10a** and **10b** are formed from either the monocyclic or bicyclic precursors (Scheme III).

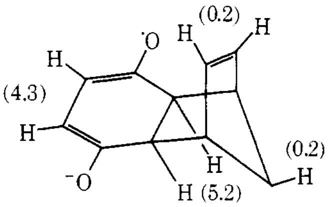
It was somewhat surprising to discover that the monocyclic 1,4-semidione **12d** was the only paramagnetic species detected when the bicyclic acetoxy ketone in the 3,7,7-trimethylbicyclo[4.1.0]hept-2-ene system was treated with base in DMSO. Apparently the oxidation–reduction and valence isomerization reactions of Scheme IV are involved. Treatment of the acetoxy ketone with 2 equiv of potassium hydroxide in methanol produced mainly the bicyclic hydroxy ketone (45%) but 3% of the monocyclic unsaturated 1,4-dione could be isolated together with traces of the unsaturated bicyclic 1,4-dione and the saturated monocyclic



10a



10b



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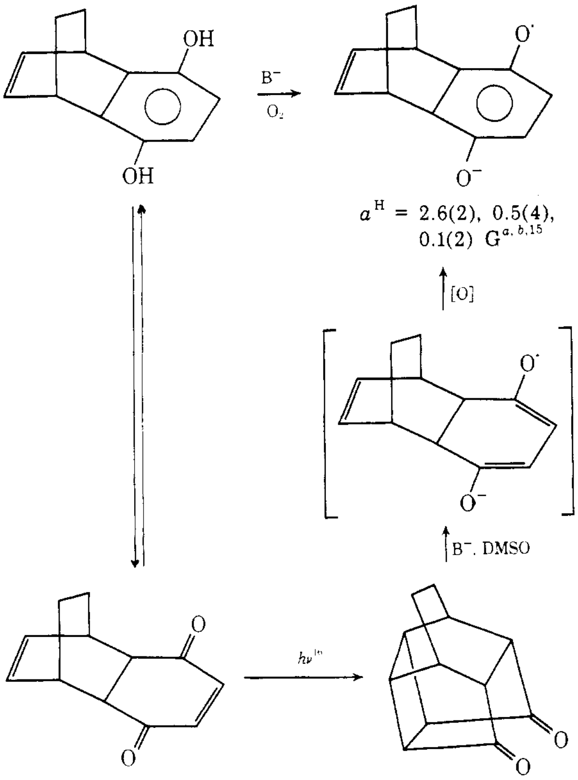
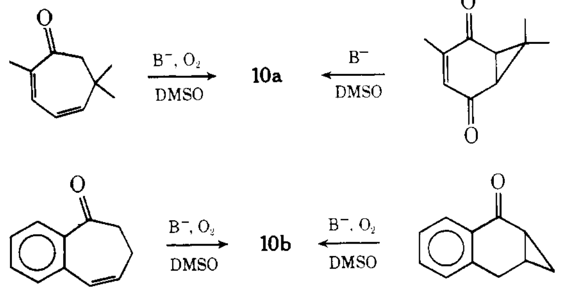
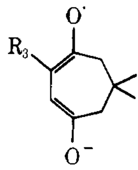
Scheme II



[a] G. A. Russell, G. W. Holland, and K.-Y. Chang, *J. Amer. Chem. Soc.*, **89**, 6629 (1967). [b] D. Kosman and L. M. Stock, *Tetrahedron Lett.*, 1511 (1967).

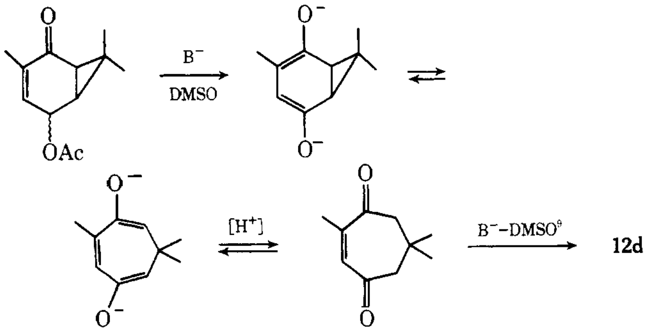
Scheme III





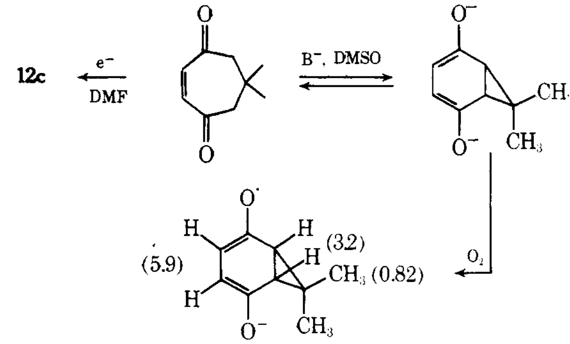
12a, $R_1 = R_2 = R_3 = H$; $a^H = 4.9$ (2), 2.6 (4) G (DMF)
b, $R_1 = R_3 = H$, $R_2 = CH_3$; $a^H = 4.9$ (2), 1.8 (2), 3.4 (2) G (DMF)
c, $R_3 = H$, $R_1 = R_2 = CH_3$; $a^H = 4.7$ (2), 2.3 (4) G (DMF)
d, $R_1 = R_2 = R_3 = CH_3$; $a^H = 2.8$, 2.0 (4); $a_{CH_3}{}^H = 5.0$ (DMSO)

Scheme IV



1,4-dione, by the oxidation-reduction sequence previously considered by Wenkert and Yonder.[19] Semidione **12d** was also produced when the monocyclic unsaturated hydroxy ketone was treated with strong base (Scheme I, example f). The reactions of Scheme IV are reversible. This was easily demonstrated under oxidative conditions. Thus, when 6,6-dimethylcyclohept-2-ene-1,4-dione was treated with base in DMSO and a trace of oxygen the bicyclic semidione **10c** was observed (Scheme V).

Scheme V

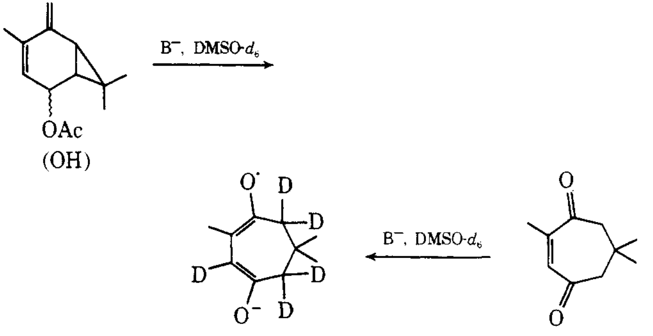


10c

a^H in G

Treatment of the bicyclic acetoxy or hydroxy ketone or the monocyclic diketone with base in DMSO-d_6 gave **12e** (Scheme VI). Exchange of the hydrogen atom at C-3 would

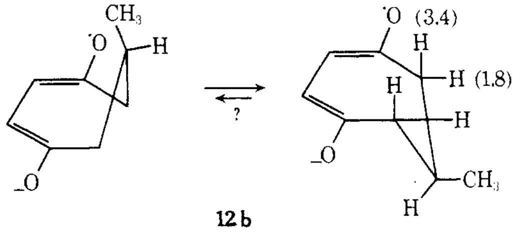
Scheme VI



12e, $a^H = 4.98$ (3) G
$a^D = 0.41$ 0.28 (4) G

be expected for the bicyclic or monocyclic dianions of Scheme IV *via* protonation and keto-enol equilibration. However, if the system is entered at a more highly oxidized stage, **10a** can be formed without hydrogen-deuterium exchange. Thus, Δ^3-2,5-carenedione in basic DMSO-d_6 gave **10a** without any hydrogen-deuterium exchange. Immediate oxygenation of eucarvone in DMSO-d_6 also gave **10a** without deuterium incorporation.

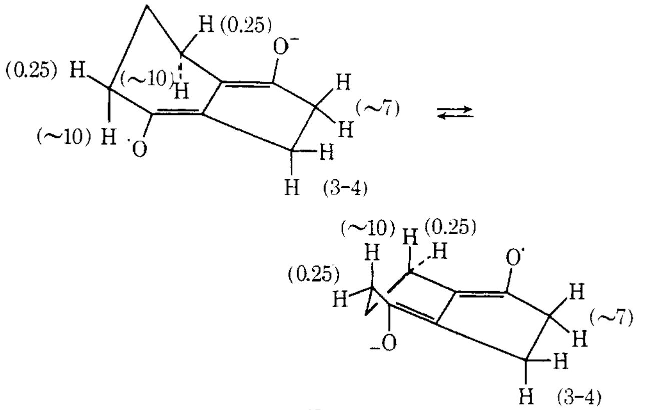
Semidiones **12a-c** were prepared by the electrolytic reduction of the unsaturated monocyclic 1,4-diones in DMF. The monosubstituted semidione **12b** shows a definite non-



12b

planar conformational preference. For the semidiones **12a**, **c**, and **d** there is no preferred conformation and apparently conformational lifetimes are $<10^{-6}$ sec at 30° since the α-hydrogen atoms are completely time averaged. These semidiones have not been studied at low temperatures.

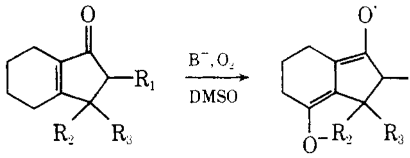
A number of 1,4-semidiones have been prepared in the hydrindan and decalin series in which a carbonyl group is located in each ring in a transoid arrangement. Oxidation of 7-keto-8-hydrindenes in basic DMSO solution produced the 1,4-semidiones **13** as deduced from the observed esr spectra (Chart I). We conclude that **13a** is conformationally rigid at 30° (conformational lifetimes $>10^{-7}$ sec) and that the observed hfsc should be assigned as shown (**13a**). In **13d** the



13a

presence of the *gem*-dimethyl substituents reduces the conformational lifetime and nearly complete time averaging of the four methylene hydrogens in the six-membered ring occurs (Figure 1).

Chart I



13

13a, $R_1 = R_2 = R_3 = H$; $a^H = 9.90$ (2), 7.10 (2), 4.20 (2), 0.25 (2) G
b, $R_1 = R_2 = H$, $R_3 = CH_3$; $a^H = 9.80$, 9.60, 7.50, 6.10, 3.50, 0.25 (2) G
c, $R_1 = CH_3$, $R_2 = R_3 = H$; $a^H = 9.85$, 9.70, 6.40, 4.40, 3.75, 0.25 (5) G
d, $R_1 = H$, $R_2 = R_3 = CH_3$; $a^H = 7.0$ (2), 4.75 (4) with line width alternation

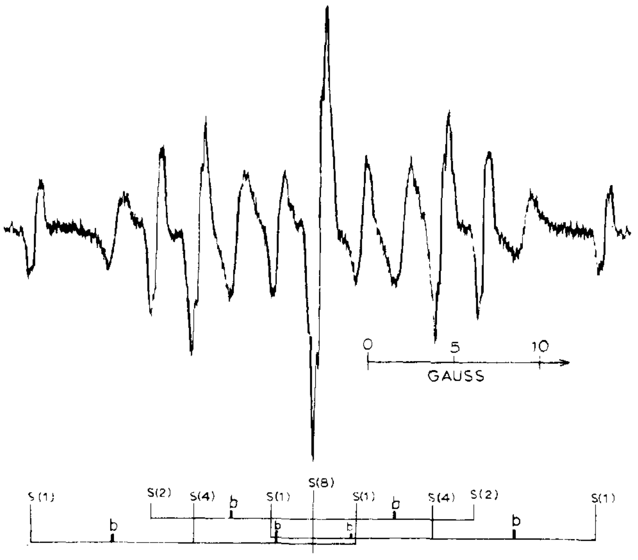
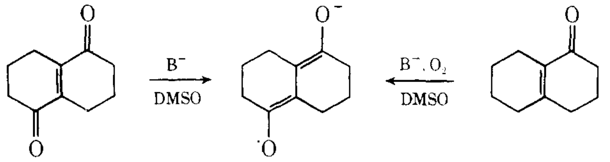


Figure 1. First derivative esr spectrum of **14d** in DMSO at 25°. The stick diagram indicates the intensities expected for lines not broadened by conformational motion in the six-membered ring (s) and the positions of the broadened lines (b) above the coalescence temperature. The cyclopentane hydrogens are presumed to be magnetically equivalent, $a^H = 7.0$ G.

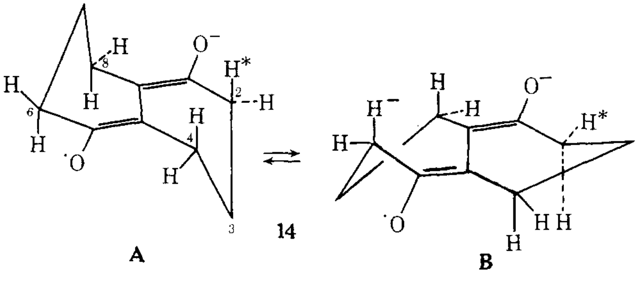
The inequality of the hydrogens in the six-membered ring of **13a–c** because of a conformational effect was nicely born out in a study of the 1,5-diketo-Δ^9-decalin derivative, **14**, which could be formed from either the α,β-unsaturated mono- or diketone (Scheme VII).

Scheme VII



14

Semidione **14** at 0–30° showed extensive line width alternation (Figure 2). At −50° an esr spectrum consistent with a frozen conformation (*i.e.*, conformational lifetime $>10^{-7}$ sec) was observed while at 105° complete time averaging of α-hydrogens had occurred to give a nine-line multiplet ($a^H \simeq 4.3$ G) with some additional fine splitting. When generated in DMF at −50° by electrolytic reduction of the dione, **14** gave pentets of pentets ($a^H = 1.8$ (4) and 7.2 (4) G) with some additional hfs of the hydrogen atom at C-3 and C-7 (0.2 G). The 4-axial-type hydrogen atoms in the conformations **A** and **B** (C-2, 4, 6, 8) have $a^H \sim 7.2$ while the



equatorial-type hydrogens at C-2, 4, 6, 8 have $a^H \sim 1.8$ G. The fine structure observed at 0° indicates that the time-averaged a^H for hydrogen atoms at C-2,4 and C-6,8 are not exactly equivalent.

Introduction of four trigonal atoms in the decalin nucleus as in **15–17** does not lead to semidiones as stable as the isomeric structures **13** and **14**. Semidione **16** has apparently been observed in low yield by the oxidation of cholestane-3,6-dione in basic DMSO[5,20] and in the present work by the treatment of 4-cholestene-3,6-dione with potassium *tert*-butoxide in DMSO. The spectrum of total width 24.2 G is consistent with $a^H \simeq 9.3$, 5.4, 5.4, 2.5, and 1.6 G. Treatment of $\Delta^{1,9}$-10-methyl-2-octalone with a trace of oxygen in basic DMSO gave a complex spectrum of total width 25.75 G which appears to be a mixture of radicals in which **15** may be present. The same esr signal was observed when $\Delta^{1,9}$-10-methyloctalin-2,8-dione was treated with base and DMSO. Oxidation of the isomeric Δ^8-10-methyl-1-octalone failed to give an esr signal in DMSO. Semidione **17** seems to be clearly involved in the oxidation of *A*-norcoprostane-2,6-dione[20,21] in basic solution. The hfsc of 7.11 (3), 4.74, and 1.24 G[6] can be assigned by analogy with **14** as 7.1 G for $a_{CH_2}{}^H$ in the A-ring, $a_{=CH}{}^{*H} = 4.74$ and $a_{CH_2}{}^H = 7.11$ and 1.24 in the B-ring. The most reasonable assignment of hfsc for **16** would be $a_{CH_2}{}^H = 9.3$ and 1.6 G in the A-ring (consistent with **13** and **14**), $a_{=CH}{}^H = 5.4$ and $a_{CH_2}{}^H = 5.4$ and 2.5 in the B-ring. As judged by the hfsc the B-rings in **15–17** and in the semidione of 7,11-diketodihydrolanosteryl acetate (Scheme I) must have grossly different conformations from the A-ring in **15–16** or the six-membered rings in **13** and **14**.

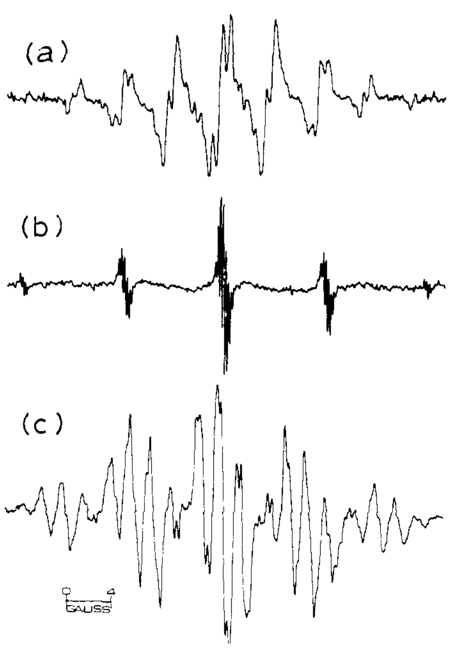
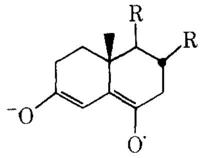
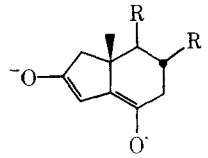


Figure 2. First derivative esr spectrum of **14** obtained by oxidation of $\Delta^{9,10}$-1-octalone in the presence of potassium *tert*-butoxide: (a) DMSO at 100°, (b) DMSO (80%)-*t*-BuOH (20%) at 0°, (c) DMF at −50°. Similar spectra were observed by treatment of $\Delta^{9,10}$-1-octalin-1,5-dione with potassium *tert*-butoxide in DMSO, a trace of oxygen being required to obtain a highly resolved spectrum similar to (b).

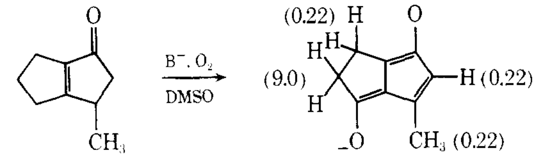


15, R = H
16, cholestane
nucleus



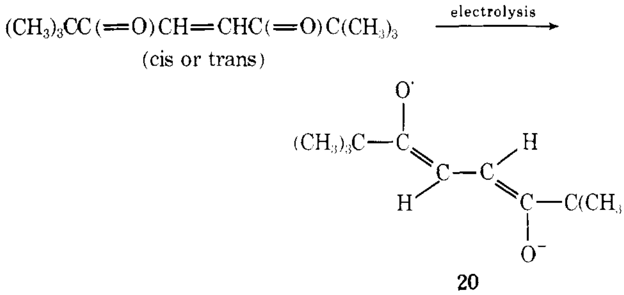
17
A-norcholestane
nucleus

Oxidation of **18** in basic DMSO gave an esr spectrum with $a^H = 9.0$ (2 H) and 0.22 G (6 H). In order to explain the hfs by six hydrogen of 0.22 G, it seems necessary to postulate that the methyl group is attached to a vinyl carbon atom. Semidione **19** is a likely possibility.



18 **19**

The spin density at C-2,3 in the 1,4-semidione system calculated from the hfsc for **15–17** is (4.74–5.40)/$Q_{\mathrm{CH}}{}^{\mathrm{H}}$ = 0.20–0.23. This is supported by the spectrum observed for **20.** There is apparently no appreciable effect on spin densities at the vinyl carbon atoms in the acyclic transoid conformation (**20**), the cyclic (cis) 1,4-semidiones **1** and **12**, the cis, trans, cis arrangement of **13**, **14**, or the cis, trans, trans stereochemistry of **15–17**. Spin densities at the carbonyl carbon atoms in the 1,4-semidione can be calculated from the hfsc of the methylene hydrogen in **1** or **12** by the relationship,[22] $a^{\mathrm{H}} = 40\rho_{\mathrm{CO}}{}^{\mathrm{C}}\cos^2 30°$ as ~ 0.1. This spin density predicts a maximum value of $a_\alpha{}^{\mathrm{H}}$ of ~4 G (for $\theta = 0°$), well below the values of ~10 G observed for axial hydrogen atoms in **13**, **15**, and **16**, of ~7 G observed in **14**, or of 9.3 and 4.7 G observed for the methylene groups in the dimeric D-ring 1,4-semidione of Scheme I. Apparently the spin distribution in these 1,4-semidiones can be considerably altered by distortion from an exactly coplanar arrangement and $\rho_{\mathrm{CO}}{}^{\mathrm{C}}$ could be as high as 0.25 in **13–19**. There is, of course, a second dihedral angle to be considered in these systems and if it deviates significantly from the tetrahedral value the $\cos^2\theta$ relationship may be inadequate.[23]


$$(\mathrm{CH_3})_3\mathrm{CC}(=\mathrm{O})\mathrm{CH}=\mathrm{CHC}(=\mathrm{O})\mathrm{C}(\mathrm{CH_3})_3 \xrightarrow{\text{electrolysis}}$$

20

a^{H} = 5.5 (2), 0.2 (18) G in DMF

Experimental Section

Reagents. *cis-* **and** *trans-***2-Acetoxypulegone** (precursors to **2b**) were prepared[24] and separated by glpc (15% XF-1150 column at 168°). The pmr spectra were consistent with those previously reported.[25]

2,2-Dimethylcyclopentane-1,3-dione, mp 46–47° (lit.[26] mp 45–47°), and **2,2-dimethyl-4-cyclopentene-1,3-dione,** bp 60° at 0.5 Torr (lit.[26,27] bp 90° at 44 Torr), precursors to **7a**, were prepared according to literature procedures.[26,27]

2,2-Dimethyl-^{13}*C*-cyclopentane-1,3-dione was prepared using methyl iodide containing ~3% ^{13}C. The product, mp 44.5–46.5, had mass spectrum (16 eV) *m/e* (rel intensity) 126(100) 127(18). **2,2,4-Trimethyl-4-cyclopentene-1,3-dione** (precursor to **7b**) was prepared by the reaction of diazomethane with 2,2-dimethyl-4-cyclopentene-1,3-dione.[26,27] Purification by glpc (5% SE-30 at 150°) gave material with a pmr ($\mathrm{CCl_4}$) δ 6.86 (q, J = 2 Hz, 1), 2.11 (d, J = 2 Hz, 3), and 1.12 (s, 6).

4-Methyl-1,2,4-triazoline-3,5-dione (precursor to **9**) was prepared as described by Stickler and Pirkle,[28] mp 96–98° (lit.[28] mp 98.0–98.5°).

Eucarvone and **Δ^3-carene-2,5-dione** (precursors to **10a**) were prepared according to the literature.[29] The 2,3-benzylcyclohept-4-enone and 3,4-benzobicyclo[4.1.0]heptan-2-one (precursors to **10b**) used have been described elsewhere.[6] Δ^3-2-Acetoxycaren-5-one (precursor to **10d**) was obtained as a viscous oil after treatment of eucarvone with lead tetracetate according to the method of Ellis.[6,30] Chromatography on silica gel and elution with hexane (90%)–ethyl acetate (10%) gave the acetoxy ketone, mp 76–78°, in 29% yield: ir (KBr) 1727, 1650, 1240 cm^{-1}; pmr ($\mathrm{CCl_4}$) δ 1.12 (s, 3), 1.27 (s, 3), 1.72–1.41 (m, 2), 1.78 (t, 3, J = 1.5 Hz), 2.06 (s, 3), 5.30–5.51 (m, 1), 6.23–6.45 (m, 1); mass spectrum (70 eV) *m/e* (rel intensity) 208 (1), 166 (50), 148 (150).[31]

Cyclohept-2-ene-1,4-dione (precursor to **12a**) was prepared according to the literature.[32,33] Material isolated by glpc (10% QF-1 column at 145°) had ir (neat) 1665, 1615 cm^{-1}; pmr ($\mathrm{CCl_4}$) δ 2.0–2.2 (m, 2), 2.6–2.9 (m, 4), 6.33 (s, 2); mass spectrum (70 eV) *m/e* 124 (parent ion).

6,6-Dimethylcyclohept-2-ene-1,4-dione (precursor to **10c** or **12c**) was prepared by the addition of diphenylsulfonium isopropylide[34] to the *p*-benzoquinone-cyclopentadiene 1:1 Diels-Alder adduct. Reduction with lithium in liquid $\mathrm{NH_3}$ gave a crystalline solid (Diels-Alder adduct of cyclopentadiene and 6,6-dimethylcyclohept-2-ene-1,4-dione) which was decomposed in glpc at 200° (15% Carbowax 20M) and the dione purified by the same glpc column at 150°. There was obtained a 50% overall yield of the unsaturated dione: ir (neat) 1670, 1615 cm^{-1}; pmr ($\mathrm{CCl_4}$) δ 1.12 (s, 6), 2.62 (s, 4), 6.34 (s, 2); mass spectrum (70 eV) *m/e* 152 (parent ion).

4-Hydroxy-2,6,6-trimethylcyclohept-2-enone (precursor to **12d**) was prepared according to the literature by selenium dioxide oxidation of 2,6,6-trimethylcyclohept-4-enone (α-dihydroeucarvone)[35]: ir (neat) 3460, 1680, 1045 cm^{-1}; pmr ($\mathrm{CCl_4}$) δ 1.0, 1.1, 1.75 ($\mathrm{CH_3}$), 2.0–2.5 ($\mathrm{CH_2}$), 4.2 (OH, $\mathrm{D_2O}$ exchangeable).

6-Methylcyclohept-2-ene-1,4-dione (precursor to **12b**) was prepared by the reaction of diphenylsulfonium ethylide[36] with the Diels–Alder adduct of cyclopentadiene and *p*-benzoquinone to yield a mixture (by pmr) of 18% *syn*- and 82% *anti*-12-methyltetracyclo[4.4.0.1^{3,4}.1^{7,10}]dodec-8-ene-2,5-dione from which the pure anti isomer crystallized: mp 127–128°; ir (KBr) 1686, 1675 cm^{-1}; pmr ($\mathrm{CDCl_3}$) δ 1.26, 1.07–1.55 (d and m, 5, J = 5.6 Hz), 1.98 (d, 2, J = 4.8 Hz), 2.08–2.54 (m, 1), 3.07–3.25 (m, 2), 3.25–3.49 (m, 2), 6.06 (t, 2, J = 1.6 Hz); mass spectrum (70 eV) *m/e* 202.[31]

4-Methyltricyclo[5.4.0.1^{8,11}]dodec-9-ene-2,6-dione was prepared from 500 mg (2.5 mmol) of *anti*-12-methyltetracyclo[4.4.-0.1^{3,4}.1^{7,10}]dodec-8-ene-2,5-dione in 12 ml of THF by addition of 350 mg (50.5 mmol) of lithium in 100 ml of liquid ammonia. Ammonium chloride (5.5 g) was added after 50 min and after evaporation of the ammonia water and ether was added. From the ether solution there was recovered 502 mg of the desired compound which was crystallized from ether–hexane mixture to give a product: mp 122.5–123.5°; ir ($\mathrm{CCl_4}$) 1707 cm^{-1}; pmr ($\mathrm{CDCl_3}$) δ 1.02 (d, 3, J = 6.1 Hz), 1.32–1.49 (m, 2), 1.68–2.82 (m, 5), 5.54–3.67 (m, 2), 3.61 (t, 2, J = 1.5 Hz), 6.21 (t, 2, J = 1.5 Hz); mass spectrum (70 eV), parent ion at *m/e* 204.[31]

6-Methylcyclohept-2-ene-1,4-dione was prepared by pyrolysis of 298 mg of 4-methyltricyclo[5.4.0.1^{8,11}]dodec-9-ene-2,6-dione on a Carbowax 20M (15%) glpc column at 200°. Distillation of the effluent at 80° (0.4 Torr) gave 159 mg (79%) of a yellow liquid shown by glpc to be a single component: ir (neat) 1668 and 1612 cm^{-1}; pmr ($\mathrm{CDCl_3}$) δ 1.04–1.23 (m, 3), 2.39–2.89 (m, 5), 6.46 (s, 2); mass spectrum (70 eV) *m/e* (rel intensity) 138(8), 110(5), 96(8).[31]

Δ^{8,9}-Hydrinden-5-one, 6-methyl-Δ^{8,9}-hydrinden-5-one, 7-methyl-Δ^{8,9}-hydrinden-5-one, and **7,7-dimethyl-Δ^{8,9}-hydrinden-5-one** (precursors to **13a–d**) were prepared according to the procedure of Conia and Leriverend.[37]

Δ^{9,10}-Octalin-1,5-dione (precursor of **14**) was prepared from Δ^{9,10}-octalin-1,5-diol[38] by use of $\mathrm{CrO_3}$ in acetic acid,[39] in 43% yield, mp 111–112° (lit.[38] mp 113–114°). Δ^{9,10}-1-Octalone (precursor to **14**) was prepared by adding 4.9 g of NaOH to a solution of 7.8 g of Δ^{9,10}-octal-1-ol acetate[38] in 150 ml of methanol. After stirring at 25° for 2 hr, the methanolic solution was concentrated at reduced pressure to ~25 ml and diluted with 200 ml of water. Three ether extracts (100 ml) of this solution were combined, washed with saturated aqueous NaCl, and dried with $\mathrm{MgSO_4}$. Removal of the ether at reduced pressure gave a liquid which was then dissolved in 20 ml of acetone. To this solution was added dropwise with stirring at 0° a solution of 1.1 equiv of $\mathrm{CrO_3}$ in 10 ml of $\mathrm{H_2O}$ and 4 ml of concentrated $\mathrm{H_2SO_4}$. After stirring 1 hr the mixture was warmed to room temperature and diluted with 400 ml of water. Three methylene chloride extracts (100 ml) of this solution were combined and dried with $\mathrm{MgSO_4}$. Removal of the methylene chloride at reduced pressure gave Δ^{9,10}-octalone which was purified by glpc (QF-1 column at 180°): ir (neat) 1660, 1629 cm^{-1}

(lit.[40] 1664 and 1634 cm^{-1}); mass spectrum (70 eV) *m/e* 150 (parent ion).

$\Delta^{1,9}$-10-Methyl-2-octalone (precursor to **15**) was prepared according to the literature,[41] bp 98–102° (0.4 Torr) (lit.[41] bp 111–112° at 2.5 Torr).

$\Delta^{8,9}$-10-Methyl-1-octalone was prepared by the *s*-collidine dehydrochlorination of 9-chloro-10-methyl-1-decalone at 160°: pmr (CCl_4) δ 0.99 (CH_3), 6.11 (t, J = 4.0 Hz, $=CHCH_2-$). The 9-chloro-10-methyl-1-decalone was prepared from 10-methyl-1-decalone.[42]

***trans*-2,2,7,7-Tetramethyl-4-octene-3,6-diones** (precursor to **20**) was prepared according to a literature procedure[43] from 2,2,7,7-tetramethyl-4,5-epoxyoctane-3,6-dione obtained from α-bromopinacolone. Reduction of the epoxide with iodide in acetic acid gave the trans enedione: mp 109.6–110.1 (lit.[43] 109–110°); pmr (CCl_4) δ 1.20 (s, 18), 7.26 (s, 2); ir (KBr) 1669, 980 cm^{-1}. *cis*-2,2,7,7-Tetramethyl-4-octene-3,6-dione (precursor to **20**) was obtained by photolysis of the trans olefin as a 3% pentane solution in quartz at 2530 Å (40 min).[44] The product was recrystallized from 95% ethanol: mp 44–45° (lit.[44] 43–45°); pmr (CCl_4) δ 1.14 (s, 18), 6.45 (s, 2); ir (KBr) 1695, 1615, 1020, 1010 cm^{-1}.

Reaction of Δ^3-2-acetoxycaren-5-one with Base. A solution of the acetoxy ketone (4.8 mmol) and KOH (9.6 mmol) in 150 ml of methanol was refluxed for 15 min. The mixture was cooled, treated with 250 ml of saturated aqueous NaCl, and extracted three times with ether. The ether extracts were washed with water and saturated aqueous NaCl and dried over $MgSO_4$. Removal of the ether at reduced pressure left a yellow oil which was dissolved in 10 ml of CCl_4 and cooled to −10°. Δ^3-2-Hydroxycaren-5-one crystallized (0.32 g, 45%), mp 82–85° (lit.[29] mp 84–86°). Evaporation of the filtrate in 0.5 ml followed by glpc (15% FFAP at 180°) gave 22 mg (3%) of 2,6,6-trimethylcyclohept-2-ene-1,4-dione[20] (pmr (CCl_4) δ 1.13 (s, 6), 1.98 (d, 3, J = 2.0 Hz), 2.53 (s, 2), 2.62 (s, 2), 6.29–6.42 (m, 1)), 2.3 mg (0.3%) of Δ^3-carene-2,5-dione,[29] and 2.2 mg (0.3%) of 2,6,6-trimethylcycloheptane-1,4-dione[29] (pmr (CCl_4) 0.92–1.20 (m, 9), 2.50 (s, 4), 2.13–2.82 (m, 3); mass spectrum (70 eV) *m/e* (rel intensity) 168 (1), 150 (1), 148 (1), 83 (6)).

Electron Spin Resonance Techniques. The apparatus and techniques have been previously described.[6] Where not otherwise specified the base was potassium *tert*-butoxide and the solvent DMSO.

Acknowledgment. Samples of the mono- and di-7-methyl-$\Delta^{8,9}$-hydrinden-5-ones and of 4-methyl[3.3.0]-1(5)-octen-2-one (precursor to **19**) were obtained from Professor Conia.[37] $\Delta^{1,9}$-10-Methyloctalin-2,8-dione (precursor to **15**) and 4-cholestene-3,6-dione (precursor to **16**) were supplied by Dr. Malhotra.[45]

References and Notes

(1) Application of Electron Spin Resonance Spectroscopy to Problems of Structure and Conformation. XXVIII. Work supported by grants from the National Science Foundation, Army Research Office (Durham), and the National Institutes of Health.

(2) Gulf Oil Fellow, 1970–1971.

(3) National Aeronautics and Space Administration Predoctoral Fellow, 1965–1968; Petroleum Research Fund Fellow, 1968–1969.

(4) National Institutes of Health Postdoctoral Fellow, 1969–1971.

(5) G. A. Russell, E. R. Talaty, and R. H. Horrocks, *J. Org. Chem.*, **32**, 353 (1967).

(6) G. A. Russell, R. L. Blankespoor, K. D. Trahanovsky, C. Chung, P. R. Whittle, J. Mattox, C. L. Myers, R. Penny, T. Ku, Y. Kosugi, and R. S. Givens, *J. Amer. Chem. Soc., in press.*

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

(8) G. A. Russell and R. L. Blankespoor, *Tetrahedron Lett.*, 4573 (1971).

(9) (a) S. F. Nelsen, *J. Amer. Chem. Soc.*, **89**, 5256 (1967); (b) S. F. Nelsen, *J. Org. Chem.*, **38**, 2693 (1973).

(10) G. A. Russell and P. Bruni, *Tetrahedron*, **26**, 3449 (1970).

(11) G. A. Russell and R. D. Stephens, *J. Phys. Chem.*, **70**, 1320 (1966).

(12) G. A. Russell and P. R. Whittle, *J. Amer. Chem. Soc.*, **89**, 6781 (1967); G. A. Russell, G. W. Holland, K.-Y. Chang, K. Stanley, K. Schmitt, R. Blankespoor, Y. Kosugi, and J. Mattox, *ibid.*, **96**, 7237 (1974).

(13) However, a value of $a_{CH_3}{}^H$ = 0.9 G is reported for **5**, X = NCH_3[9a] and a value of $a_{CH}{}^H$ = 2.26 G for **5**, X = $CHCH_3$.[9b]

(14) G. A. Russell, T. Ku, and G. Lokensgard, *J. Amer. Chem. Soc.*, **92**, 3833 (1970).

(15) S. F. Nelsen and B. M. Trost, *Tetrahedron Lett.*, 5737 (1966).

(16) R. E. Cookson, E. Crundwell, H. H. Hill, and J. Hudec, *J. Chem. Soc.*, 3062 (1964).

(17) H. E. Zimmerman, D. S. Crumrine, D. Döpp, and P. W. Huyffer, *J. Amer. Chem. Soc.*, **91**, 434 (1969).

(18) See also S. F. Nelsen and J. P. Gillespie, *J. Org. Chem.*, **38**, 3592 (1973).

(19) G. E. Wenkert and J. E. Yonder, *J. Org. Chem.*, **35**, 2986 (1970).

(20) W. G. Dauben, G. A. Boswell, and W. Templeton, *J. Org. Chem.*, **25**, 1853 (1960).

(21) A. Windaus, *Z. Physiol. Chem.*, **117**, 146 (1921).

(22) G. A. Russell, E. T. Strom, E. R. Talaty, and S. A. Weiner, *J. Amer. Chem. Soc.*, **88**, 1998 (1966).

(23) G. A. Russell, *Tech. Chem.*, **4** (1), 441 (1972).

(24) L. H. Zalkow and J. W. Ellis, *J. Org. Chem.*, **29**, 2626 (1964).

(25) L. H. Zalkow, J. W. Ellis, and N. R. Brennan, *J. Org. Chem.*, **28**, 1705 (1963).

(26) W. C. Agosta and A. B. Smith, *J. Org. Chem.*, **35**, 3856 (1970).

(27) W. C. Agosta and A. B. Smith, *J. Chem. Soc. D*, 685 (1970).

(28) J. C. Stickler and W. H. Pirkle, *J. Org. Chem.*, **31**, 3444 (1966).

(29) E. J. Corey and H. J. Burke, *J. Amer. Chem. Soc.*, **78**, 174 (1956).

(30) J. W. Ellis, *J. Org. Chem.*, **34**, 1154 (1969).

(31) Discrepancies between experimental and calculated elemental compositions were: % C < 0.25%, % H < 0.15%.

(32) A. C. Cope, T. A. Liss, and G. W. Wood, *J. Amer. Chem. Soc.*, **79**, 6287 (1957).

(33) O. L. Chapman and D. J. Pasto, *J. Amer. Chem. Soc.*, **82**, 3642 (1960).

(34) E. J. Corey, M. Jautelat, and W. Oppolzer, *Tetrahedron Lett.*, **24**, 2325 (1967); E. J. Corey and M. Jautelat, *J. Amer. Chem. Soc.*, **89**, 3912 (1967).

(35) J. R. B. Campbell, A. M. Islam, and R. A. Raphael, *J. Chem. Soc.*, 4096 (1956).

(36) V. Franzen, H. Schmidt, and C. Mertz, *Chem. Ber.*, **94**, 2942 (1961).

(37) J.-M. Conia and M.-L. Leriverend, *Bull. Soc. Chim. Fr.*, 2891 (1970).

(38) W. P. Campbell and G. C. Harris, *J. Amer. Chem. Soc.*, **63**, 2721 (1941).

(39) C. H. DePuy and E. F. Zaweski, *J. Amer. Chem. Soc.*, **81**, 4920 (1959).

(40) H. O. House and H. W. Thompson, *J. Org. Chem.*, **26**, 3729 (1961).

(41) N. C. Ross and R. Levine, *J. Org. Chem.*, **29**, 2341 (1964).

(42) H. O. House, R. W. Giese, K. Kronberger, J. P. Kaplan, and J. F. Simeone, *J. Amer. Chem. Soc.*, **92**, 2800 (1970).

(43) M. Charpentier-Morize, *Bull. Soc. Chim. Fr.*, 960 (1962).

(44) R. Ramassuel and A. Rassat, *Bull. Soc. Chim. Fr.*, 2218 (1963).

(45) S. K. Malhotra, J. J. Hostynek, and A. F. Lundin, *J. Amer. Chem. Soc.*, **90**, 6565 (1968).