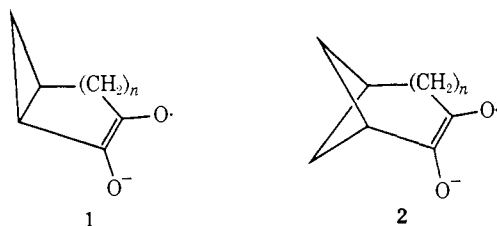


Aliphatic Semidiones.

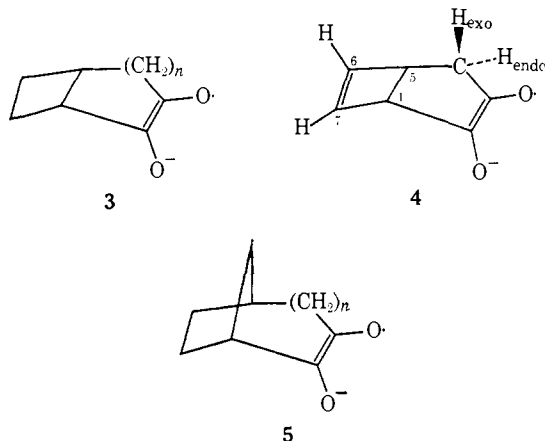
XXIV. Bicyclo[*n*.2.0]alkane-2,3-semidiones¹Glen A. Russell,* Philip R. Whittle,² C. S. C. Chung, Y. Kosugi, Kirk Schmitt, and Edward Goettert*Contribution from the Department of Chemistry, Iowa State University, Ames, Iowa 50010. Received May 16, 1974*

Abstract: Several bicyclo[3.2.0]heptane-2,3-semidiones and bicyclo[3.2.0]hept-6-ene-2,3-semidiones are reported including derivatives in the β -lumicolchicine, lumiisocolchicine, and dihydrolumiisocolchicine series as well as in the tricyclo[3.3.2.0^{1,5}]decane and decene systems. INDO calculations are reported for bicyclo[3.2.0]hept-6-ene-2,3-semidione as well as for the isomeric bicyclo[3.2.0]hept-2-ene-6,7-semidione and compared with experimental results. Homoallylic delocalization of the electron spin between the two π systems does not appear to be important in either of the isomers.

We have previously reported on the esr spectra of bicyclo[*n*.1.0]- and bicyclo[*n*.1.1]alkane-2,3-semidiones (1 and 2).^{3,4} In the present work we consider



saturated (3) and unsaturated (4) semidiones containing the bicyclo[*n*.2.0] ring system while in a following publication⁵ various derivatives of bicyclo[*n*.2.1]alkane-semidiones (5) are considered. With $n = 0$ the semi-



diones have not been detected in series 1 or 3 whereas 2 and 5 with $n = 0$ are easily observed. Extended-Hückel-SCF calculations have been reported for the unobserved bicyclo[2.1.0]pentane- and bicyclo[2.2.0]hexanesemidiones as well as for other cyclobutanesemidiones.⁶ In Table I are given the results of INDO calculations^{7,8} for bicyclo[3.2.0]hept-6-ene-2,3-semidi-

(1) Work supported by a grant from the National Science Foundation.
(2) National Aeronautics and Space Agency Predoctoral Fellow, 1965-1968; Petroleum Research Fund Fellow, 1968-1969.

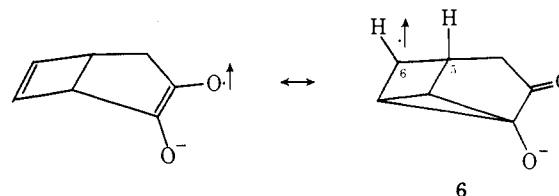
(3) G. A. Russell, J. J. McDonnell, P. R. Whittle, R. S. Givens, and R. G. Keske, *J. Amer. Chem. Soc.*, **93**, 1452 (1971).

(4) G. A. Russell, P. R. Whittle, and R. G. Keske, *J. Amer. Chem. Soc.*, **93**, 1467 (1971).

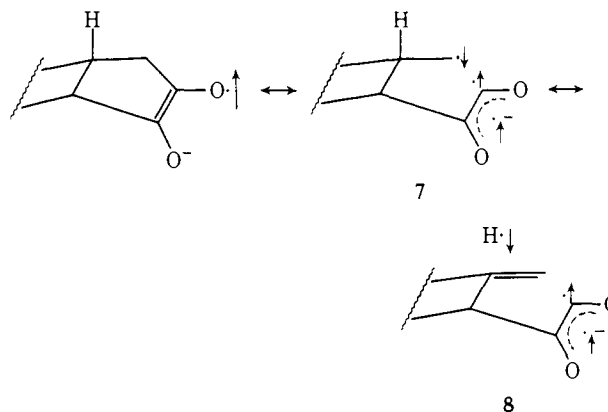
(5) G. A. Russell, G. W. Holland, K.-Y. Chang, R. G. Keske, J. Mattox, C. S. C. Chung, K. Stanley, K. Schmitt, R. Blankespoor, and Y. Kosugi, *J. Amer. Chem. Soc.*, in press.

(6) G. A. Russell, P. R. Whittle, R. G. Keske, G. Holland, and C. Aubuchon, *J. Amer. Chem. Soc.*, **94**, 1693 (1972).

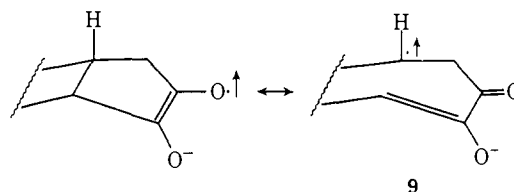
one for the geometry specified in Figure 1. The negative value calculated for a_6^H suggests that positive spin density at C-6 is to be expected, at least at low values of α , by a homoallylic interaction 6. Hyperconjugation



of positive spin density at C-6 with C(5)-H should produce a positive value of a_5^H . The negative value predicted for a_5^H by the INDO method increases in magnitude as θ becomes larger (*i.e.*, as 6 becomes less important) and seems to be best interpreted as resulting from spin polarization of the C(3)-C(4) bond followed by hyperconjugation of C(5)-H with the induced negative spin density, structures 7 and 8. Carbon atom 5



can also obtain positive spin density *via* carbon-carbon hyperconjugation (structure 9) which could be rational-



(7) J. A. Pople, D. L. Beveridge, and P. A. Dobash, *J. Amer. Chem. Soc.*, **90**, 4201 (1968); D. L. Beveridge, P. A. Dobash, and J. A. Pople, *J. Chem. Phys.*, **48**, 4802 (1968).

(8) G. R. Underwood and V. L. Vogel, *J. Amer. Chem. Soc.*, **93**, 1058 (1971).

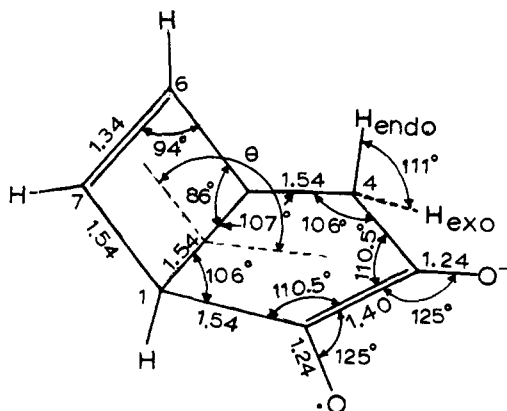


Figure 1. Geometry used for INDO calculations for **4**; all hydrogens were positioned with $d(\text{C-H}) = 1.08 \text{ \AA}$ so that all H-C-C angles for a given hydrogen atom were equal.

Table I. Hyperfine Splitting Constants (a^H in G) Calculated for **4** by the INDO Method

Position	θ			
	102°	108°	114°	130°
H-1	3.0	3.9	4.8	7.1
H-4(endo)	3.6	4.0	4.2	4.5
H-4(exo)	4.0	5.0	5.6	6.3
H-5	0.03	-0.28	-0.46	-0.60
H-6	-0.63	-0.41	-0.27	-0.13
H-7	0.48	0.48	0.48	0.40

ized with either a positive or negative value of a_5^H .⁹ Although **9** is probably not very important because of stereoelectronic restrictions (the carbon-carbon bond is nearly orthogonal to the carbonyl p_z orbital), it is easily rationalized that a_5^H is quite sensitive to the geometry as the calculations indicate.

Experimentally the prediction of strong hfs by three α hydrogen atoms is easily verified for **3** ($n = 1$) and **4**. Bicyclo[3.2.0]heptan-2-one and the isomeric 3-ketone gave a weak esr spectrum with $a^H = 16.3, 10.7, 10.7 \text{ G}$ when treated with a trace of oxygen in basic DMSO.¹⁰ The semidione was quite unstable and the minor hfsc could not be resolved. Radical anions more stable were formed when 1,4,4-trimethyl[3.2.0]heptane-2,3-dione or dihydrolumisocolchicine ketol¹¹ were treated with base and DMSO, or when tricyclo[3.3.2.0^{1,5}]decan-2-one was treated with a trace of oxygen in basic DMSO solution. The only consistent assignment of hfsc seems to be the one given in structures **10-13** (Chart I). The fairly strong and quite stereoselective hfs by the exo hydrogen at C-7 is consistent with the W-plan interactions noted in numerous semidiones.^{3-6,9,12,13}

An attempt to prepare the tricyclic derivative of **10** has been reported.³ Acyloin condensations of dimethyl bicyclo[2.1.0]pentane-endo,endo-dicarboxylate led not to the expected tricyclo[3.2.0.0^{4,6}]heptane-2,3-semidione

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

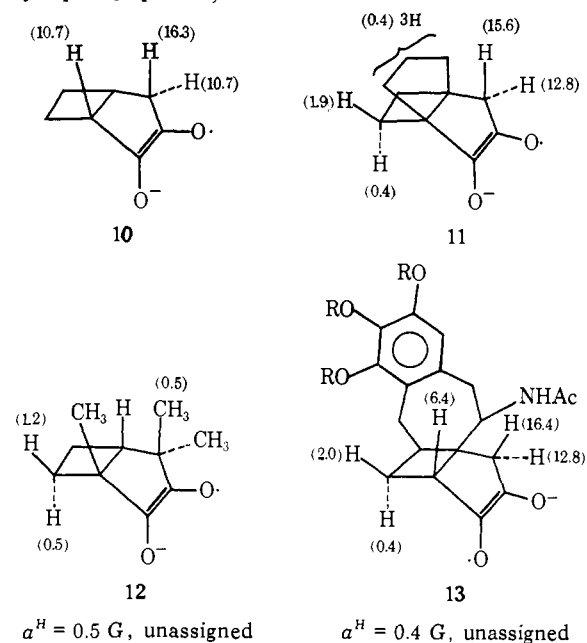
(10) G. A. Russell, E. R. Talaty, and R. H. Horrocks, *J. Org. Chem.*, **32**, 353 (1967).

(11) O. L. Chapman, H. G. Smith, and P. A. Barks, *J. Amer. Chem. Soc.*, **85**, 3171 (1963).

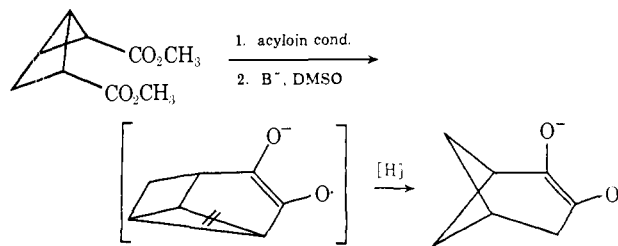
(12) G. A. Russell and K.-Y. Chang, *J. Amer. Chem. Soc.*, **87**, 4381 (1965).

(13) G. A. Russell, K.-Y. Chang, and C. W. Jefford, *J. Amer. Chem. Soc.*, **87**, 4381 (1965).

Chart I. Assignment of Hfsc (G) to Bicyclo[3.2.0]heptane-2,3-semidiones



but instead to ring-opened bicyclo[3.1.1]heptane-2,3-semidiones.^{3,4}

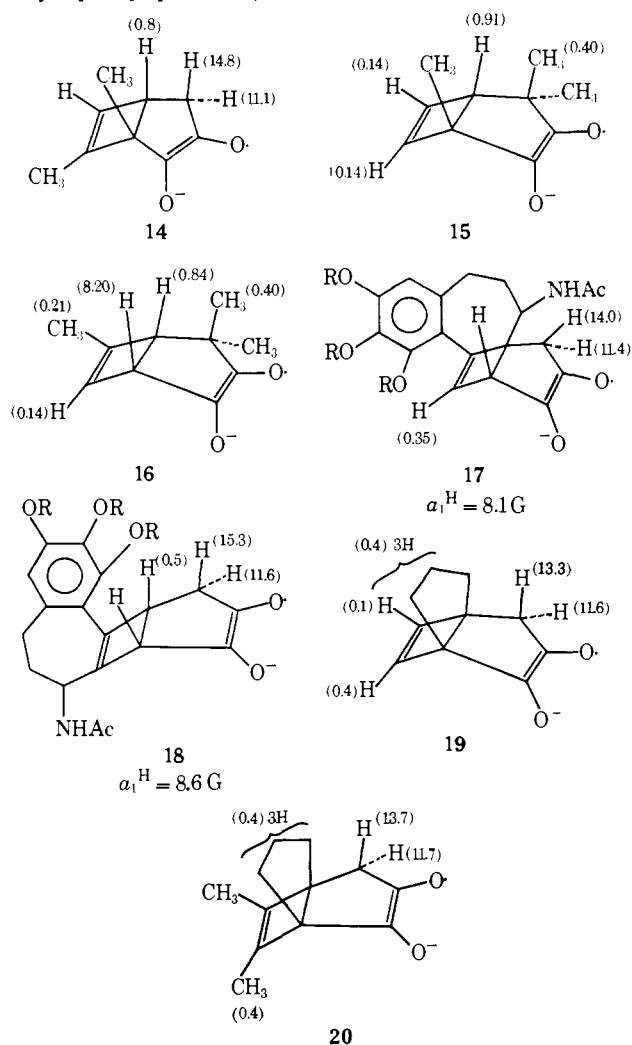


Derivatives of **4** were prepared by oxidation of 1,7-dimethylbicyclo[3.2.0]hept-6-en-2-one, tricyclo[3.3.2.0^{1,5}]dec-9-en-2-one, and 9,10-dimethyltricyclo[3.3.2.0^{1,5}]dec-9-en-2-one, by the disproportionation of lumiisocolchicine ketol or β -lumisocolchicine ketol or by the reduction of 1,4,4-trimethylbicyclo[3.2.0]hept-6-ene-2,3-dione or oxidation of 1,4,4-trimethylbicyclo[3.2.0]hept-6-en-1-one in basic DMSO solution. The only consistent assignment of hfsc seems to be that given in Chart II.

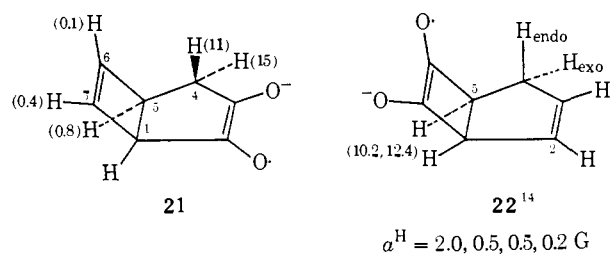
In DMSO- d_6 **17** and **19** lost two α hydrogen atoms ($a^H = 13-14, 11.5 \text{ G}$) to give spectra with $a^D = 2.1-2.2, 1.7 \text{ G}$. The hydrogen with the largest hfsc (exo) was exchanged more readily as had been previously noted in the bicyclo[3.1.0]hexane-2,3-semidione.³ As in the case of bicyclo[3.1.0]hexane-2,3-semidione, the bridgehead hydrogen atoms in **17** and **19** were not significantly exchanged even after 24 hr. The hfs predicted for H(6) is not seen although the hfs predicted for H(5) is routinely detected in bicyclo[3.2.0]hept-6-ene-2,3-semidiones. It may be that the presence of the double bond at C(6)-C(7) increases the contribution of structure **9** so that a_5^H is more important in **14-16**, or **18** than in **12**.

The composite of hfsc from **14-20** yield the hfsc given in **21** for the parent bicyclo[3.2.0]hept-6-ene-2,3-semidione. It is of interest to compare the hfsc of the

Chart II. Assignment of Hfsc (G) to Bicyclo[3.2.0]hept-6-ene-2,3-semidiones



isomeric bicyclo[3.2.0]hept-2-ene-6,7-semidione (**22**)¹⁴ with **21**.



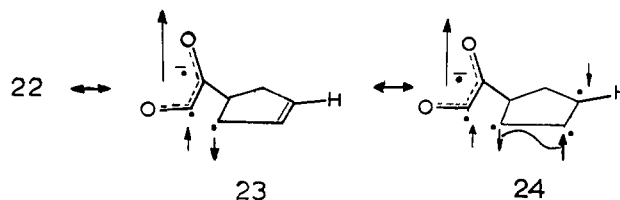
INDO calculations for **22** according to the geometry of Figure 2 are summarized in Table II. Since the

Table II. INDO Calculations of Hfsc (G) for Bicyclo[3.2.0]hept-2-ene-6,7-semidione (**22**)

Atoms	θ		
	120°	130°	140°
H-1	10.2	12.0	13.7
H-2	0.2	0.1	0
H-3	1.5	1.5	1.4
H-4(endo)	-0.5	-0.6	-0.7
H-4(exo)	-0.4	-0.5	-0.6
H-5	9.1	11.2	13.2

(14) G. A. Russell and K. Schmitt, *J. Amer. Chem. Soc.*, **94**, 8918 (1972).

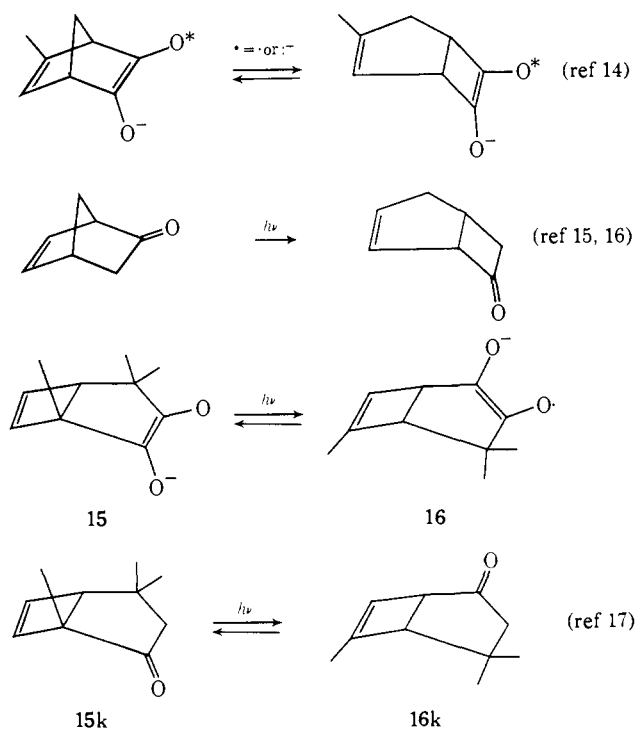
values of a^H calculated for **22** are not particularly sensitive to geometry it appears safe to assign the experimental values as $a_2^H = 0.2$, $a_3^H = 2.0$, and $a_{4\text{-endo}}^H = a_{4\text{-exo}}^H = 0.5$ G. The calculated value of a_3^H for **22** is strongly positive indicative of a negative spin density on C-3 whereas for **21** (Table I) a_6^H is negative, at least at low values of θ . It appears that for **22** the homoallylic interaction (6) is less important than spin polarization in the C(7)–C(1) bond followed by conjugation of the negative spin density with the double bond, structures **23**, **24**. This interaction must occur for **21** also



and in fact at $\theta = 160^\circ$, a_6^H in **21** becomes positive indicating that **23**, **24** predominate over **6**. Further examples of the nearly equivalent (but of opposite sign) interactions in homoallylic systems are provided by studies of spin labels with different orbital symmetries in the bicyclo[2.2.1]heptadiene and bicyclo[2.2.2]octadiene systems.⁵

Semidiones **15** and **16** were examined carefully in search of a 1,3-sigmatropic rearrangement which would interconvert them (Chart III). There was no evidence

Chart III



of a thermal conversion of $16 \rightleftharpoons 15$ at 25° over a period of several hours in DMSO solution. Photolysis of semidione **15** (prepared by oxidation of monoketone)

(15) D. I. Schuster, M. Axebrod, and J. Auerbach, *Tetrahedron Lett.*, 1911 (1963).

(16) D. E. Bays and R. C. Cookson, *J. Chem. Soc. B*, 226 (1967).

(17) G. Büchi and E. M. Burgess, *J. Amer. Chem. Soc.*, **82**, 4333 (1960).

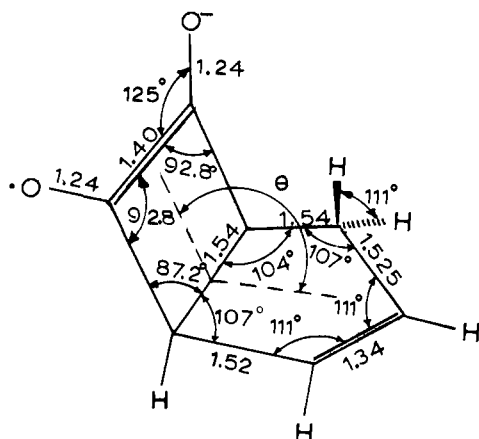
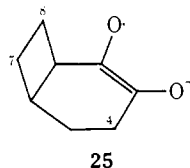


Figure 2. Geometry used in INDO calculations for **22**; hydrogen atoms were positioned so that $d(\text{C-H}) = 1.08 \text{ \AA}$ and all CCH angles for a given hydrogen atom were equal.

by uv in the esr cavity caused the semidione to gradually decay. A solution of semidione **16**, prepared by the *in situ* oxidation of **16k**, when irradiated with uv rapidly gave about equal parts of semidiones **15** and **16** (see Figure 3 for typical spectra). However, this may be the result of a photochemical conversion of **16k** to **15k**, the photochemical stationary state favoring **15k**.¹⁷ However, the photoconversion of **16k** to **15k** is not particularly efficient. Under our conditions *in situ* irradiation of **16k** in DMSO directly in the esr cavity followed by treatment with potassium *tert*-butoxide in the dark, yielded only semidione **16**. It appears that the photochemical conversion of **16** into **15** was observed.

Bicyclo[4.2.0]octane-2,3-semidione (**25**) was prepared



by the treatment of *endo*- and *exo*-3-acetoxycyclohexane-2-one with potassium *tert*-butoxide in DMSO. The major hfs involved three hydrogen atoms with $a^{\text{H}} = 8.4 \text{ G}$ assigned to H-1, H-4(*exo*), H-4(*endo*). The equivalence of the hydrogens at C-4 suggests that the six-membered ring is quite planar with a dihedral angle for the α hydrogen atoms intermediate between those observed for axial hydrogens ($a^{\text{H}} = 13.2 \text{ G}$) and equatorial hydrogens ($a^{\text{H}} = 6.0 \text{ G}$) in cyclohexane-semidione.¹⁸ Other hfs observed for **25** are $a^{\text{H}} = 0.55$ (4 hydrogens) and 0.30 G . A possible assignment of the 0.55-G splitting is to H-5(*exo*), H-5(*endo*), H-6, and H-8(*exo*) with the 0.30-G splitting assigned to H-8(*endo*). The assignment of the *exo* and *endo* hfs at C-8 is made by analogy with the hfs observed at C-7 in the bicyclo[3.2.0]heptane-2,3-semidiones described previously.

Bicyclo[4.2.0]octane-3,4-semidione (**26**) was prepared from *cis*-1,2-bis(carbomethoxymethyl)cyclobutane¹⁹ by acyloin condensation in the presence of trimethylchlorosilane.²⁰ The esr spectrum gave triplets (2 H)

(18) G. A. Russell, G. R. Underwood, and D. C. Lini, *J. Amer. Chem. Soc.*, **89**, 6636 (1967).

(19) E. Vogel, *Justus Liebigs Ann. Chem.*, **615**, 1 (1958).

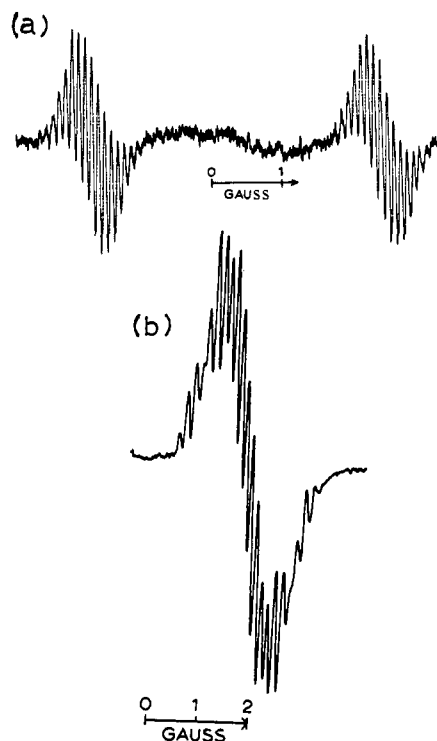


Figure 3. First derivative esr spectra of (a) semidione **16** prepared by oxidation of 4,4,6-trimethylbicyclo[3.2.0]hept-6-en-2-one; (b) semidione **15** prepared by reduction of 1,4,4-trimethylbicyclo[3.2.0]hept-6-ene-2,3-dione or oxidation of 1,4,4-trimethylbicyclo[3.2.0]hept-6-en-2-one. Spectra were recorded in DMSO at 25° in the presence of 0.1 M potassium *tert*-butoxide.

of 10.25, 4.40, and 0.37 G . The two largest hfs were replaced by $a^{\text{D}} = a^{\text{H}}/6.5$ in $\text{DMSO-}d_6$. The 0.37-G splitting seems most likely to be the *exo* hydrogens at C-7,8 in the staggered conformation. This assignment agrees well with the assignments made in systems **27-30**,²¹ (Chart IV).

Experimental Section

General Procedure for Generation of Semidiones. Semidiones were prepared from bis(trimethylsiloxy)alkenes by mixing equal volumes of well-deaerated solutions of the bis(trimethylsiloxy)alkene (0.2 M) and potassium *tert*-butoxide (0.4 M) in DMSO. In a typical experiment 1 ml of chlorotrimethylsilane followed by 0.1–0.2 mmol of the pure diester were added to a suspension of 0.2 ml of sodium–potassium alloy (1:3) in 25 ml of ether at 0° (nitrogen atmosphere). The mixture was stirred vigorously under nitrogen for 1–3 hr and filtered, and the ether was removed *in vacuo*. The residue was taken up in 0.5 ml of DMSO, deaerated by bubbling nitrogen through the solution in one leg of an inverted U-shape mixing cell,²² mixed with an equal volume of a deaerated solution of potassium *tert*-butoxide (0.2 M) in DMSO from the other leg of the mixing cell, and shaken into a Varian V-4548 aqueous solution cell. The admission of traces of air to this solution often improved the quality of the esr spectrum. Monoketones, diketones, and α -ketols were treated in a similar fashion, *i.e.*, dissolved in DMSO, deaerated, mixed with basic DMSO, and oxygenated if necessary.

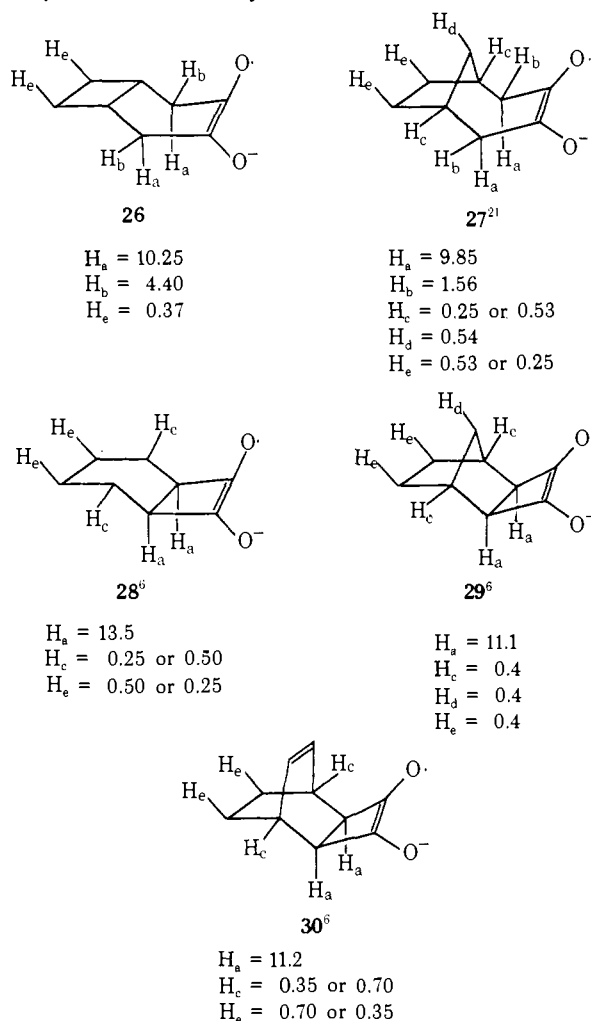
1,4,4-Trimethylbicyclo[3.2.0]heptane-2,3-dione. Precursor of 12. To a solution of 2.5 g (0.016 mol) of 1,4,4-trimethylbicyclo[3.2.0]heptan-2-one¹⁷ in 20 ml of 95% ethanol was added 2.0 g (0.018 mol) of selenium dioxide and the mixture refluxed for 12 hr. The mixture was cooled, 100 ml of methanol added, and the suspension of selenium removed by filtration over a Celite column. After dis-

(20) G. A. Russell and P. R. Whittle, *J. Amer. Chem. Soc.*, **89**, 6781 (1967).

(21) Unpublished results of Dr. R. G. Keske.

(22) G. A. Russell, E. G. Janzen, and E. T. Strom, *J. Amer. Chem. Soc.*, **86**, 1807 (1964).

Chart IV. Assignment of Hfsc (G) in Some Rigid Bicyclic and Tricyclic Derivatives of Cyclooctanesemidiones



tilation of the solvent the residue was chromatographed on silica gel whence the diketone was eluted with ether (2%)–hexane (98%). Sublimation (50° at 10 Torr) and recrystallizations (pentane) gave 1.2 g (45%) of bright orange crystals: mp 57–58°; ir (CCl₄) 1765, 1750 cm⁻¹; pmr (CCl₄) δ 1.01 (s, 3), 1.39 (s, 3), 1.5–2.8 (m, 5); mass spectrum (70 eV) *m/e* 166 (parent ion), 138, 123, 109.

Dihydrolumiisocolchicine Ketol. Precursor of 13. Lumiisocolchicine ketol¹¹ in 5 ml of 95% ethanol was hydrogenated with 1 atm of hydrogen and 5 mg of Adams catalyst for 42 hr. Filtration and evaporation of the ethanol left a residue which could be crystallized from benzene to give the desired product, mp 140–145° (lit.¹¹ mp 146–149°).

1,7-Dimethylbicyclo[3.2.0]hept-6-en-2-one. Precursor of 14. 2-Cyclopentenone (5 g) in 100 ml of 2-butyne was degassed under nitrogen at 0° for 10 min and then irradiated in a quartz vessel containing an internal cooling coil at 3000 Å in a Rayonet photochemical reactor for 90 hr. Distillation gave a fraction, bp 59–63° (12 Torr), shown by glpc to contain ~80% of the desired ketone and 20% of the isomeric 6,7-dimethylbicyclo[3.2.0]hept-6-en-2-one.^{23,24} Higher boiling fractions contained almost exclusively the latter ketone. 1,7-Dimethylbicyclo[3.2.0]hept-6-en-2-one was obtained by preparative glpc (15% Carbowax 20M, 130°): ir (CCl₄) 1630, 1720, 3030 cm⁻¹; pmr (CCl₄) δ 1.14 (s, 3), 1.57 (t, 3, *J* = 1.5 Hz), 1.7–3.0 (m, 5), 5.85 (t, 1, *J* = 1.5 Hz); mass spectrum (70 eV) *m/e* 136 (parent ion); 2,4-dinitrophenylhydrazone mp 170–172° (lit.²³ mp 171–172°).

1,4,4-Trimethylbicyclo[3.2.0]hept-6-ene-2,3-dione. Precursor of 15. A solution of 2.5 g (0.017 mol) of 1,4,4-trimethylbicyclo[3.2.0]hept-6-en-2-one¹⁷ and 2.0 g (0.018 mol) of selenium dioxide in

20 ml of 95% ethanol was refluxed for 26 hr. Methanol was added and the suspension of selenium removed by filtration over a Celite column. After distillation of the solvent the residue was chromatographed on silica gel to give 150 mg (5%) of the yellow diketone eluted by ether (5%)–hexane (95%). Recrystallization from pentane gave a material with mp 75–76°; ir (CCl₄) 1770, 1750, 1660 cm⁻¹; pmr (CDCl₃) δ 1.02 (s, 3), 1.20 (s, 3), 1.53 (s, 3), 2.90 (s, 1), 5.86 (d, 1, *J* = 2.5 Hz), 6.50 (d, 1, *J* = 2.5 Hz); mass spectrum (70 eV) *m/e* 164 (parent ion) 136, 121, 108, 107.

β-Lumicolchicine Ketol. Precursor to 18. β-Lumicolchicine was reduced to the alcohol with sodium borohydride and hydrolyzed with dilute acid to the ketol,^{25,26} mp 215–218° (lit.²⁶ mp 208°).

Tricyclo[3.3.2.0^{1,5}]dec-9-en-2-one. Precursor of 19. A solution of 7 g of bicyclo[3.3.0]oct-1(5)-en-2-one (Badische Anilin and Soda-Fabrik) and 100 ml of 1,2-dichloroethylene (~75% *cis*) in 500 ml of pentane was degassed with nitrogen for 1 hr and then irradiated in a Pyrex cell with a Hanovia 550-W lamp until the 1695-cm⁻¹ absorption (enone) was completely replaced by a 1740-cm⁻¹ absorption. The solvent was removed *in vacuo* to give a residue which was treated with 4.5 ml of ethylene glycol and 50 mg of *p*-toluenesulfonic acid in benzene. This solution was refluxed for 12 hr with separation of water by a Dean-Stark trap. The product was shaken with saturated aqueous sodium chloride and dried (MgSO₄) to yield after concentration a mixture of ketals (15 g). The ketals in 125 ml of ether and 350 ml of liquid ammonia were treated with 5 g of sodium added over a 15-min period. The mixture was stirred for 2 hr before treatment with an excess of ammonium chloride followed by water. The solution was extracted by ether; the ether extract was washed with water and saturated aqueous sodium chloride and dried (MgSO₄) before removal of the ether *in vacuo* to give 9.6 g of an orange oil. The oil was stirred for 5 hr with a mixture of 40 ml of ether and 20 ml of 3 *N* hydrochloric acid. The ether layer was separated, washed, dried (MgSO₄), and distilled *in vacuo* to give the tricyclic ketone, bp 83–84° (10 Torr), which was further purified by glpc (15% Carbowax 20M 150°); ir (CCl₄) 1725, 1675 cm⁻¹; pmr (CCl₄) δ 0.8–3.5; semicarbazone, mp 187–190° dec (lit.²⁷ mp 185° dec).

Tricyclo[3.3.2.0^{1,5}]dec-9-en-2-one. Precursor of 11. A solution of 1 g of tricyclo[3.3.2.0^{1,5}]dec-9-en-2-one in 30 ml of benzene containing 200 mg of 10% Pd on charcoal was stirred under hydrogen for 36 hr. The mixture was filtered, the benzene evaporated *in vacuo*, and the residue purified by glpc (15% Carbowax 20M, 170°) to give a material with mp 61–63°; ir (CCl₄) 1730 cm⁻¹; pmr (CCl₄) δ 1.3–3.2; semicarbazone, mp 203–206° dec (lit.²⁷ mp 200–202° dec).

9,10-Dimethyltricyclo[3.3.2.0^{1,5}]dec-9-en-2-one. Precursor of 20. A solution of 7.6 g of bicyclo[3.3.0]oct-1(5)-en-2-one and 10 g of 2-butyne in 120 ml of benzene was deoxygenated with nitrogen before irradiation in a Rayonet reactor at 15° for 14 days. The product was vacuum distilled to give 7.4 g of material, bp 94–95° (8 Torr), which was purified by glpc (20% DEGS, 170°); ir (CCl₄) 1725, 1680 cm⁻¹; pmr (CCl₄) δ 1.0–3.3; semicarbazone, mp 217° dec (lit.²⁸ mp 214° dec).

Bicyclo[4.2.0]octan-2-one. Precursor to 25. The desired ketone was synthesized by the low temperature (–70°) photolysis of 2-cyclohexenone and ethylene in methylene chloride²⁹ and acetoxyated with lead tetraacetate³⁰ to give a yellow oil purified by glpc (25% Carbowax 20M, 100°) to give a mixture of *endo*- and *exo*-3-acetoxybicyclo[4.2.0]octan-2-ones: ir (neat) 1725, 1745 cm⁻¹; pmr (CCl₄) δ 1.2–3.2 (m, 11), 1.99 and 1.98 (s, 3), 4.5–5.3 (m, 1); mass spectrum (70 eV) *m/e* 182 (parent).

***cis*-1,2-Bis(carbomethoxymethyl)cyclobutane.¹⁹ Precursor of 26.** 1,2-Cyclobutanecarboxylic anhydride (Aldrich Chemical Co.) was hydrolyzed to the dicarboxylic acid (mp 127–130°). Conversion to the acid chloride and hence to the diazo ketone with diazomethane gave a product which was treated with silver benzoate and triethylamine in methanol solution to give the desired diester, bp 80–85° (0.2 Torr), purified by glpc (15% Carbowax 20M, 150°); pmr (CCl₄) δ 1.5–3.0 (m, 10), 3.00 (s, 6); mass spectrum (70 eV) *m/e* 200 (parent ion), 168, 141.

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