of alcohols was oxidized with chromium trioxide as in the preparation of ketone **10** to yield 11 mg (69%) of crude ketone **32**. Analysis of the crude compound by glpc showed it to be 90% of one ketone. A small amount of the ketone was purified by preparative glpc; ir (CCl_4) 1770 cm^{-1}; mass spectrum, *m/e* 132 (M^+), 104 (M − CO).

endo,endo-**3,7-Dicarbomethoxytetracyclo[3.3.0.0^{2,8}.0^{4,6}]octane** (**33**). (a) A solution of *endo,endo*-secocubane dimethyl ester **19** (290 mg, 1.3 mmol), 3.0 g of silver nitrate, 20 ml of water, and 25 ml of methanol were refluxed under nitrogen for 2 days. The reaction mixture was cooled and diluted with 100 ml of ether. The water layer was drawn off and the ether solution dried. The solvent was removed by evaporation to give 194 mg (66%) of diester **33**: mp 87–88°; ir (CCl_4) 2935, 1735 cm^{-1}; nmr (τ, CCl_4) 6.40 (6 H, s), 6.90 (2 H, quintet, J = 2.2 Hz), 8.15 (6 H, m); mass spectrum, *m/e* 222.

Anal. Calcd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 64.84; H, 6.16.

(b) A solution of pentacyclo[4.4.0.0^{2,4}.0^{3,8}.0^{5,7}]deca-9-ene (**28**, 100 mg, 0.77 mmol) in 30 ml of ethyl acetate was treated with a 20% excess of ozone at −70°. The crude ozonide, after removal of the ethyl acetate by evaporation, was oxidized at 0° with Jones reagent.[11] The crude reaction mixture was diluted with 3 *N* sodium hydroxide and extracted with ether. The aqueous solution was acidified with 10% hydrochloric acid and extracted three times with ether. The acidic ether extracts were dried, concentrated by aspirator pressure, and treated with excess diazomethane. The 120 mg of yellow oil obtained was examined by glpc and found to contain one volatile product (30% yield from olefin **28** according to glpc estimates). A sample of this product was purified by preparative glpc and found to have the same infrared spectrum, mass spectrum, and glpc retention time as the material from part a.

Aliphatic Semidiones. XV. 2,3-Semidiones Derived from the Bicyclo[*n*.1.0]alkanes[1]

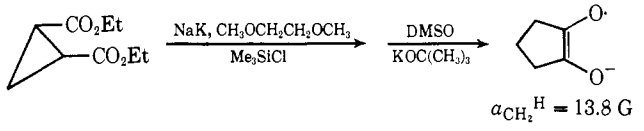
Glen A. Russell,* John J. McDonnell, Philip R. Whittle,[2] R. S. Givens,[3] and R. G. Keske[4]

Contribution from the Department of Chemistry, Iowa State University, Ames, Iowa 50010. *Received May 29, 1970*

Abstract: The synthesis of bicyclo[2.1.0]pentane-, bicyclo[3.1.0]hexane-, bicyclo[4.1.0]heptane-, bicyclo[5.1.0]octane-, and bicyclo[6.1.0]nonane-2,3-semidiones has been investigated. Acyloin condensations of *cis*-1,2-cyclopropanedicarboxylic esters failed to yield bicyclopentane semidiones. Instead, the ring-opened cyclopentanesemidiones were formed. Acyloin condensation or oxidation of the 2- or 3-ketones in basic solution produced the bicyclo[3.1.0]hexane-2,3-semidione. The hyperfine splittings observed in the esr spectrum were assigned to the six hydrogen atoms by examination of a number of deuterium and alkyl derivatives. Extended Hückel self-consistent field calculations are reported which are in excellent agreement with the experimentally observed values. During this investigation it was determined that the α-methylene group in bicyclo[3.1.0]hexanesemidione underwent a highly stereoselective hydrogen–deuterium exchange in basic dimethyl sulfoxide solution wherein the exo hydrogen exchanged much more rapidly than the endo hydrogen. It was also observed that *syn*-6-alkylbicyclo[3.1.0]-hexane-2,3-semidiones rearranged to the anti isomers with base catalysis. An electrocyclic mechanism is suggested in which the bicyclo[3.1.0]hexane ring opens to a cyclohexadienyl intermediate which undergoes competing ring closure and aromatization. Overoxidation of the bicyclo[3.1.0]hexanesemidione leads to an *o*-semiquinone with molecular rearrangement in which C-6 of the bicyclic semidione is converted to C-3 in the semiquinone. A sigmatropic 1,4 migration followed by a cyclopropanol ring opening is suggested. A variety of tricyclic derivatives containing the bicyclo[3.1.0]hexanesemidione nucleus and showing interesting long-range esr splittings have been synthesized. Bicyclo[4.1.0]heptane-2,3-semidione appears to exist in two conformations depending upon the substitution pattern. The importance of long-range interactions is greatly reduced in the bicyclo[4.1.0]heptane system and inconsequential in the bicyclo[5.1.0]octane- and bicyclo[6.1.0]nonane-2,3-semidiones.

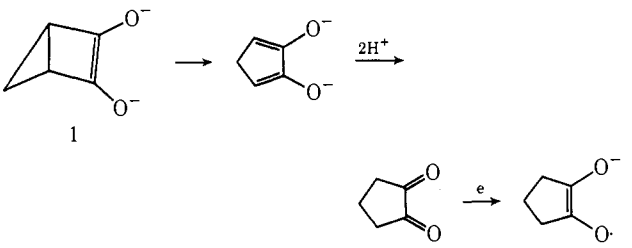
Attempts to prepare bicyclopentanesemidione (**1**) by acyloin condensation of the *cis*-cyclopropanedicarboxylic ester in the presence or absence of trimethylchlorosilane led instead to cyclopentanesemidione, detected by esr spectroscopy (Scheme I).

Scheme I



Ring opening is not surprising since the enediol derivative resulting from the acyloin condensation would be a bicyclopentene derivative. Ring opening could occur by hydrogenation with hydrogen released from traces of hydroxylic impurities. Alternately disymmetric ring opening (not allowed by orbital symmetry considerations) might precede the gain of the two hydrogen atoms (Scheme II). Ring opening also oc-

Scheme II



(1) Application of Electron Spin Resonance Spectroscopy to Problems of Structure and Conformation. XX. Supported by the Army Office of Research (Durham) and by the National Science Foundation.

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

(3) National Institute of Health Postdoctoral Fellow, 1966–1967.

(4) National Science Foundation Predoctoral Fellow, 1967–1969.

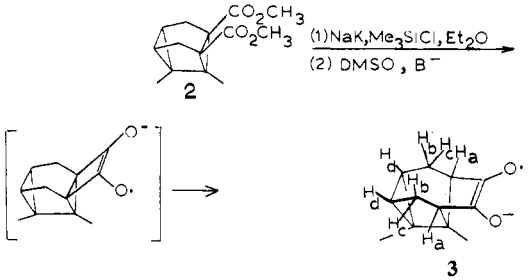
Table I. Hyperfine Splitting Constants and Assignments for Substituted Bicyclo[3.1.0]hexane-2,3-semidiones at 25° in DMSO Solution

Substituent	a_1^H	$a_{4\text{-endo}}^H$	$a_{4\text{-exo}}^H$	$a_{4\text{-exo}}^D$	a_5^H	$a_{6\text{-syn}}^H$	$a_{6\text{-anti}}^H$	Other
None, 6[a-c]	4.0	7.9	14.9	2.3	0.8	0.8	4.0	
syn-6-D, 7[c]	4.0	7.9	14.9		0.8		4.0	
6,6-Dideuterio, 8[b]	4.0	7.9	14.9		0.8		a^D = 0.7	
6,6-Dimethyl, 9[b]	5.1	7.6	14.6	2.3	0.9			$a_{6a\text{-}CH_3}$ = 0.45
anti-6-CH_3, 10[b]	4.3	7.6	14.6	2.3	0.40	0.90		$a_{6a\text{-}CH_3}$ = 0.40
syn-6-CH_3, 11[b]	4.6	7.4	14.3		1.1		1.5	
anti-6-C_2H_5, 12[b]	4.2	7.8	14.6	2.3	0.35			$a_{6a\text{-}CH_2}$ = 0.75
anti-6-C_2H_5-1-D, 13[b]	a_1^D = 0.7	7.8	14.7	2.3	0.35			$a_{6a\text{-}CH_2}$ = 0.75
anti-6-Methoxymethyl, 14[c]	4.2	7.8	14.7		0.35			$a_{6a\text{-}CH_2}$ = 0.75
1-Methyl, 15[b]		7.8	14.6		0.8	0.8	4.2	
5-Methyl, 16[b]	3.8	7.6	14.2				3.8	
5-Isopropyl, 17[b]	4.0	8.2	14.5			0.7	3.7	$a_{CH<}$ = 0.30
1-C_2H_5-5-CH_3, 18[b]		7.6	14.3				4.4	
1-Isopropyl-4-*endo*-CH_3, 19[b]			13.85	2.2	0.58	0.7	4.9	
1-Isopropyl-4-*exo*-CH_3, 20[c]		6.2			0.58	0.8	4.2	
1-Isopropyl-4-*exo*-CH_3-4-*endo*-D, 21[c]		a^D = 0.95			0.58	0.8	4.2	
1-Isopropyl-4,4-dimethyl, 22[d]					0.4	0.4	4.9	$a_{CH<}$ = 0.4
4,4-Dideuterio, 22[c]	4.0	a^D = 1.1	a^D = 2.3		0.8	0.8	4.0	
24[b]		7.9	14.4			0.7	4.4	a^H = 0.35, 0.35, 0.35
25[c]		7.6	14.6			0.7	4.4	a^H = 0.5, 0.2, 0.2
26[b]			13.5				4.6	
27[b]		7.7	13.8	1.9				$a_{6a\text{-}CH_3}$ = 1.0
28[b]		7.6	14.3	2.2				$a_{6a\text{-}CH<}$ = 1.1
29[b]	4.8	7.6	14.0	2.2				$a_{6a\text{-}CH<}$ = 1.5
30[b]		7.6	14.0					$a_{6a\text{-}CH<}$ = 1.5
31[b]	4.8	7.8	14.0					$a_{6a\text{-}CH<}$ = 1.5
32[b]	4.8	7.8	14.0					$a_{6a\text{-}CH<}$ = 1.5

[a] Prepared by acyloin condensation. [b] Prepared by oxidation of 2-ketone. [c] Prepared by oxidation of 3-ketone. [d] Prepared by hydrolysis and oxidation of 2-keto-3-(*n*-butylthiomethylene) derivative.

curred when the bicyclo[2.1.0]pentane system[5] was fused into system **2**, Scheme III. The 7.3-G splitting is undoubtedly associated with H_a in **3** and the three other triplet splittings are associated with the hydrogen

Scheme III

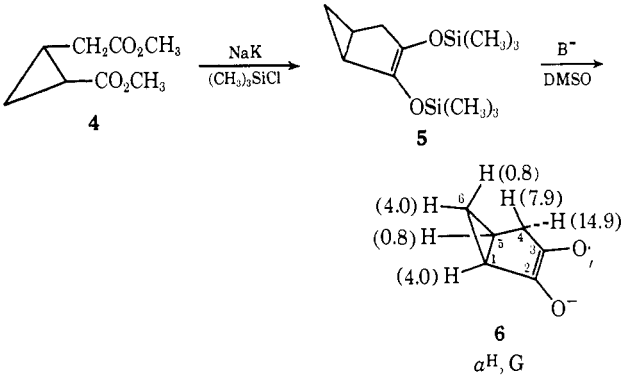


a^H = 7.3, 7.3, 1.1, 1.1, 0.6, 0.6, 0.3, 0.3

atoms shown. Hydrogen atoms H_b have a geometry similar to the endo-5,6 hydrogens in bicyclo[2.2.1]-heptane-2,3-semidione which are known to have a very weak interaction with the unpaired spin.[6] Thus, the 0.3-G triplet probably is associated with H_b and the 1.1- and 0.6-G triplets with H_c and H_d.[7]

Bicyclo[3.1.0]hexanesemidione.[8] Acyloin condensation of **4** yielded 2,3-bis(trimethylsiloxy)bicyclo-[3.1.0]hex-2-ene (**5**) which yielded[9] the bicyclo[3.1.0]-hexanesemidione (**6**) in which all of the hydrogen atoms could be detected by esr hyperfine splitting (Scheme IV). The hyperfine splittings in **6** were assigned (Table I) on the basis of the initial esr spectra for the semidiones **7–32** observed in the oxidation of the corresponding 2- or 3-ketones or in a few cases by the hydrolyses and oxidation of the α-*n*-butylthiomethylene ketone[10] (Scheme V).

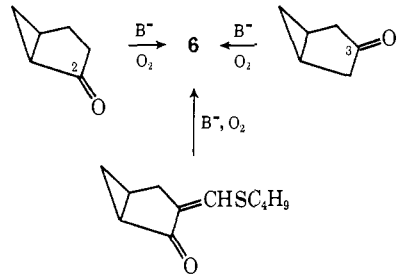
Scheme IV



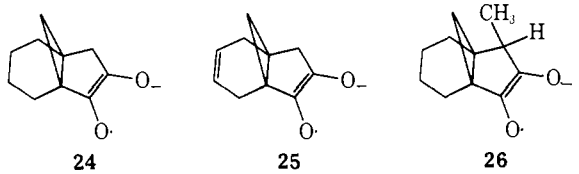
a^H, G

(5) R. Askani, *Chem. Ber.*, 98, 3618 (1965).
(6) G. A. Russell and K.-Y. Chang, *J. Amer. Chem. Soc.*, 87, 4381 (1965).
(7) Further work is in progress on the assignment of hyperfine splitting constants in blocked cyclooctanesemidione conformations: unpublished results with Mr. K. Schmitt.
(8) For preliminary communications, see G. A. Russell, P. R. Whittle, and J. McDonnell, *J. Amer. Chem. Soc.*, 89, 5515 (1967); G. A. Russell, J. McDonnell, and P. R. Whittle, *ibid.*, 89, 5516 (1967); G. A. Russell and J. J. McDonnell, *Tetrahedron Lett.*, 4213 (1968).
(9) G. A. Russell and P. R. Whittle, *J. Amer. Chem. Soc.*, 89, 6781 (1967).
(10) R. E. Ireland and J. A. Marshall, *J. Org. Chem.*, 27,1615 (1962).

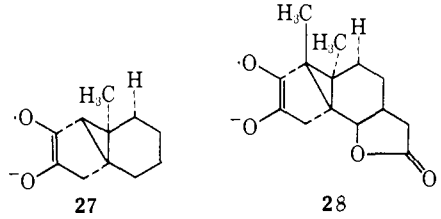
Scheme V



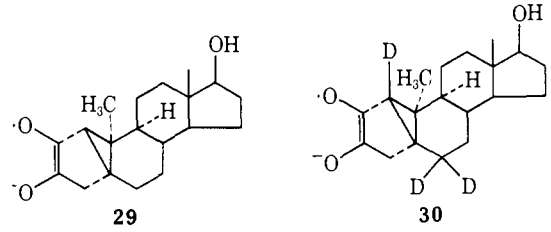
The assignment of hyperfine splitting constants for **6** was verified by EH–SCF calculations. EH calculations were previously reported for several possible geometries



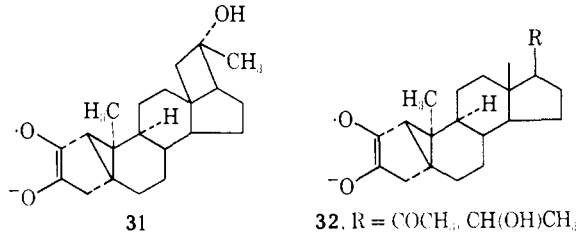
24 **25** **26**



27 **28**



29 **30**

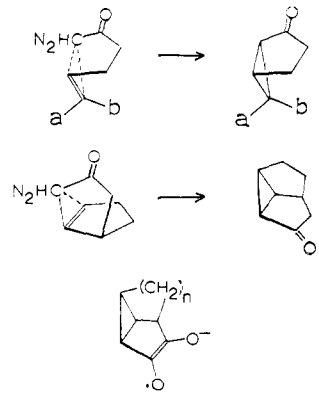


31 **32**, R = $COCH_3$, $CH(OH)CH_3$

of **6** and gave good agreement with experimental values except that the ratio of splitting of H-1:H-5 was much lower than the actual ratio of 4:1.[11] Using the geometry shown in Figure 1 and the SCF approximation of Cusachs,[12] the splitting constants listed in Figure 1 were calculated.[13]

A variety of bicyclic ketones in the bicyclo[3.1.0]-hexane system (*e.g.*, *syn*- and *anti*-6-alkyl derivatives) were prepared from the appropriate Δ^3-diazo ketone

Scheme VI

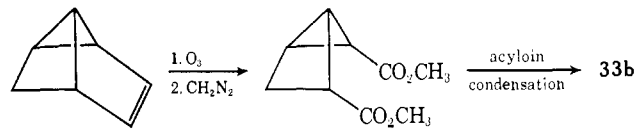


33a, n = 0
b, n = 1
c, n = 2
d, n = 3
e, n = 4

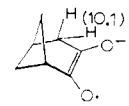
(Scheme VI).[14,15] This technique was adopted to the synthesis of the tricyclic 2-ketones which proved to be precursors to **33c–e**.[16,17]

No attempt was made to prepare the benzvalene derivative, **33a**. Compound **33b** was prepared from the tricyclic olefin (Scheme VII).[18] When the acyloin

Scheme VII



condensation was performed in the presence of trimethylchlorosilane and the crude product reacted with potassium *tert*-butoxide in DMSO, a mixture of two radicals was formed. The least stable was possibly **33b** but the hfsc of a^H = 9.95, 9.40, 3.60, 0.45, 0.35, and 0.15 G were not in good agreement with those expected on the basis of **33c–33e** or bicyclo[2.2.1]-heptanesemidione.[6] The more stable radical had hfsc of a^H = 10.10, 10.10, 3.50, 3.50, 0.35, and 0.20 G. This radical has been observed in another study and identified as bicyclo[3.1.1]heptane-2,3-semidione (**34**),[19] a hydrogenolysis product of **33b**. In DMSO-d_6 the hydrogen atoms with a^H = 10.1 G were replaced with deuterium, a^D = 1.55 G.



34

The hfsc attributed to **33b** can also be rationalized with a derivative of **34** in which a nucleophile has attacked the tricyclic precursor to yield a bicyclo[3.1.1]-heptane-2,3-semidione with a substituent at one of the methylene bridges (C-6). The observed hfsc are as-

(11) G. R. Underwood and R. S. Givens, *J. Amer. Chem. Soc.*, **90**, 3713 (1968).

(12) (a) J. H. Corrington and L. C. Cusachs, *J. Chem. Phys.*, in press; (b) L. C. Cusachs and J. H. Corrington, Yale Symposium in Sigma Molecular Orbital Theory, O. Sinanoğlu and K. Wiberg, Ed., Yale University Press, New Haven, Conn., 1970, p 256. We thank Professor Cusachs for preprints of this work.

(13) We have achieved excellent agreement between calculated and experimental hyperfine splitting constants (hfsc) in a number of other rigid bicyclic semidiones by use of this EH–SCF calculation. It appears that in these systems our ability to calculate electron delocalization and, therefore, hfsc has reached the stage that assignment by substitution procedure is no longer required provided the geometry of the radical is known reasonably well.

(14) G. Stork and J. Ficini, *J. Amer. Chem. Soc.*, 83, 4678 (1961).

(15) M. M. Fawzi and C. D. Gutche, *J. Org. Chem.*, 31, 1390 (1966).

(16) W. von E. Doering, E. T. Fossel, and R. L. Kaye, *Tetrahedron*, **21**, 25 (1965).

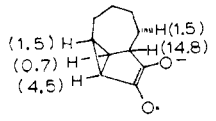
(17) S. A. Monti, D. J. Bucheck, and J. C. Shepard, *J. Org. Chem.*, **34**, 3080 (1969).

(18) P. R. Story, *J. Amer. Chem. Soc.*, 83, 3347 (1961); H. C. Brown and H. M. Bell, *ibid.*, 85, 2324 (1963).

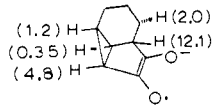
(19) G. A. Russell, P. R. Whittle, and R. G. Keske, *ibid.*, **93**, 1467 (1971).

signed as follows: 9.95 (C-4), 9.4 (C-4), 3.6 (anti, C-7), 0.45 (C-1), 0.35 (C-6), and 0.15 (C-5).

Compounds **33c–33e** were prepared by oxidation of the corresponding tricyclic ketones. The assignment of hfsc in **33e** seems straightforward by comparison with the parent bicyclo[3.1.0]hexanesemidione. Dreiding models show an excellent W-plan interaction of one of the methylene hydrogen with the carbonyl p_z orbital at C-3. A possible assignment of hfsc for

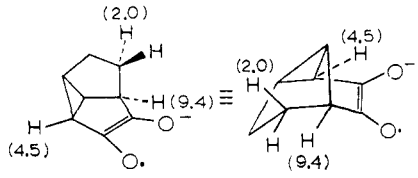


33e

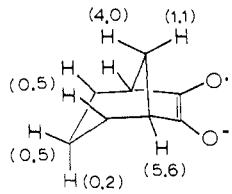


33d, three hydrogen with a^H = 0.35 G unassigned

33c emphasizes the fact that this semidione can also be considered to be the bicyclo[3.2.1]octanone derivative **35**.[20]

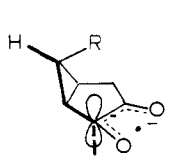


33c

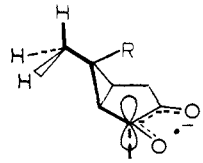


35

The long-range interactions found in bicyclo[3.1.0]-hexanesemidione and its 6-*anti*-alkyl derivatives fit the long-range, zigzag, coplanar arrangement (**36**, **37**).[6,11,20,21]

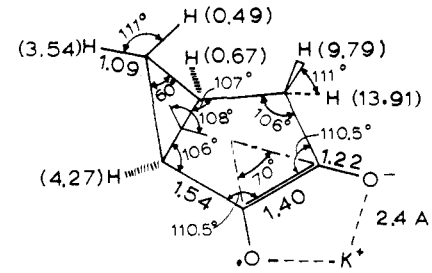


36, 2V;
R = H; a^H = 4 G
R = CH_3; a^H = 1.5 G



37, 2.5V;
R = H; a^H = 0.40 G
R = CH_3; a^H = 0.45 G

Interaction of an orbital and a bond can be shown to be more important when a trans orientation occurs.[11] Structure **38** can be considered to involve such trans interactions and would be analogous to the ordinary hyperconjugation structure (1.5 V), **39**.[22] We feel that



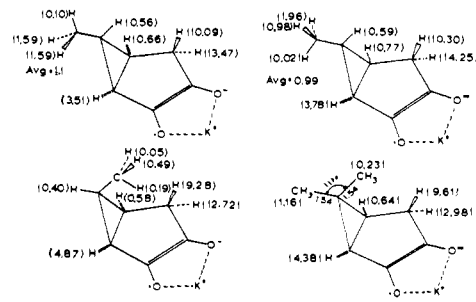
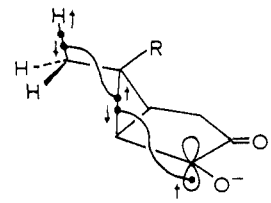
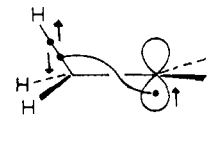


Figure 1. Geometry of bicyclo[3.1.0]hexane-2,3-semidione used in EH–SCF calculations. Methyl, methylene, and methine hydrogen atoms were placed so that for a given group all H–C–C angles were equal. Calculated hfsc (in gauss) are in parentheses.



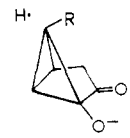
38



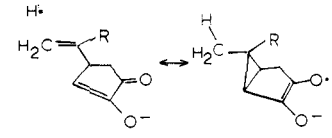
39

both interactions involve spin delocalization rather than a polarization mechanism. The EH calculations support this view since there is no mechanism provided in the EH calculation for spin polarization.

The effect of syn-6 substitution in decreasing the magnitudes of the long-range interactions is surprisingly large. This may be the result of different interaction mechanisms being involved. The effect of the *syn*-6-methyl group on decreasing the 2V interaction would appear to be consistent with homohyperconjugation structures such as **40**. On the other hand, a *syn*-6-



40



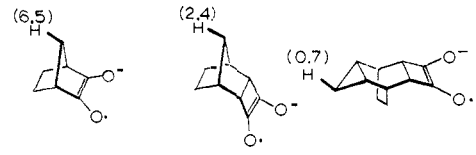
41

alkyl group would not be expected to have much of an effect on structures such as **41**.

(20) G. A. Russell, K.-Y. Chang, and C. W. Jefford, *J. Amer. Chem. Soc.*, 87, 4383 (1965); G. A. Russell, G. Holland, K.-Y. Chang, and L. H. Zalkow, *Tetrahedron Lett.*, 1955 (1967).

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

(22) This approach does not appear able of explaining integer V interactions unless spin polarization is invoked. Actually there appears to be a reasonable fall-off by a factor of about threefold for each additional bond when one progresses through the series 2V,[6] 2.5V,[9] and 3V,[23] *e.g.*



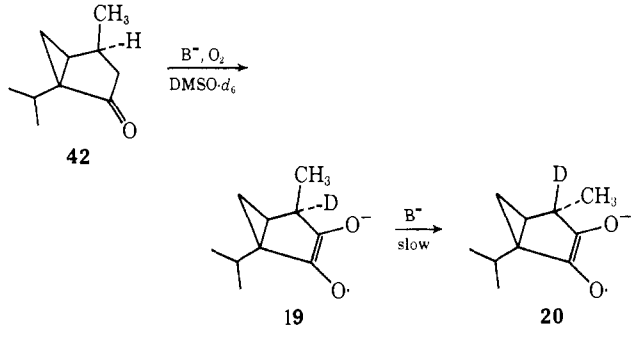
(23) Unpublished results with Dr. G. Holland.

The relative importance of **38** and **39** can be judged by the hfsc of **10** ($a_{CH_3}^{H}$ = 0.40) and *trans*-butane-2,3-semidione ($CH_3C(O\cdot)=C(O^-)CH_3$), $a_{CH_3}^{H}$ = 5.6 G.[24] The 2.5V interaction is about $^1/_{15}$th as important as the 1.5V interaction. In **10** the methyl group is undergoing free rotation so that effectively every carbon–hydrogen bond has a time-averaged dihedral angle (θ) of 45° with a reference plane.[25] However, only $^1/_2$ of the time is this dihedral angle in the zigzag arrangement of **37** (the other $^1/_2$ of the time it would form a sickle conformation). If it is assumed that in the zigzag conformation, a $\cos^2\theta$ relationship is followed, as is commonly accepted for the 1.5 interaction,[26] the rigid conformation **37** would be expected to have a^H = (0.40)(2)($\cos^2 0°/\cos^2 45°$) = 1.6 G. Values of a^H very nearly equal to this value were obtained for semidiones **29–32** (a^H = 1.5 G) where the nearly coplanar 2.5V arrangement is required by the polycyclic ring system. This long-range splitting can be useful in assigning structure to anti-6 substituted bicyclo[3.1.0]-hexane derivatives. One example of the use of this technique has already been reported.[27]

Certain aspects of the chemistry of the bicyclo[3.1.0]-hexanesemidiones have attracted our attention. These have involved the mechanism of hydrogen–deuterium exchange at C-4, the mechanism of ring opening to form *o*-semiquinones in the presence of excess oxygen, and the occurrence of a molecular rearrangement *via* ring inversion.

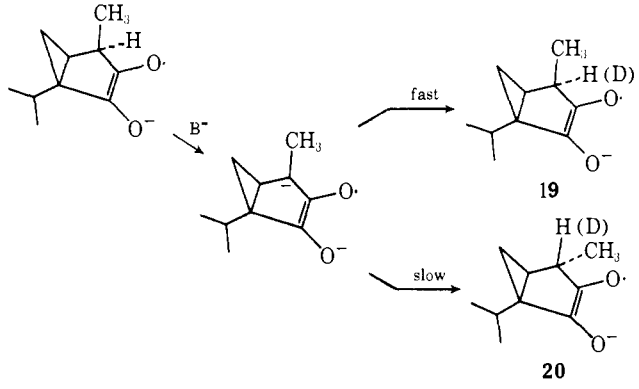
Stereoselective Hydrogen–Deuterium Exchange. The independent existence of the exo–endo isomers **19** and **20** was surprising. We had previously found that the α-hydrogen atoms in many semidiones are readily exchanged with deuterium in DMSO-d_6 although bridgehead hydrogens in the [2.2.1]bicycloheptane, [2.2.2]bicyclooctane, and [3.1.1]bicycloheptane series were not exchanged.[6] We had, therefore, expected that **19** would be rapidly epimerized into the more stable **20**. In DMSO-d_6 β-dihydroumbellulone (**42**) gave upon oxidation **19** containing a deuterium atom in the α position (Scheme VIII). Thus, epimerization at C-4 does not

Scheme VIII



necessarily accompany hydrogen–deuterium exchange. Upon standing radical anion **19** slowly epimerized to **20**; an equilibrium of about 90% **20**–10% **19** appeared to be formed. When thujone (3-ketone, *exo*-methyl) was oxidized in DMSO, the initial esr signal was the 90:10 mixture of **20**–**19**. Similar results were obtained in the acyloin condensation of dimethyl homothujadicarboxylate. In thujone, or the acyloin, the 3-ketone allows epimerization at C-4 and hydrogen–deuterium exchange to occur before semidione formation. Thus, bicyclo[3.1.0]hexan-3-one in DMSO-d_6 rapidly exchanged all α hydrogen atoms in the presence of potassium *tert*-butoxide (exchange followed by pmr). The only explanation of the results observed with β-dihydroumbellulone is that hydrogen exchange at C-4 occurs stereoselectively (Scheme IX). Protonation to

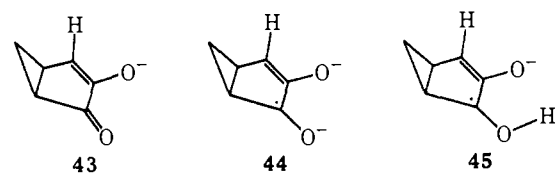
Scheme IX



give the more stable product (**20**) must be slower than protonation to yield **19**.

The oxidation of the bicyclo[3.1.0]hexanones in DMSO-d_6 provided more information. The 3-ketone yielded the 4,4-dideuteriosemidione, undoubtedly the result of exchange of the α hydrogens of the ketone. The 2-ketone gave a stereoselective exchange of the exo hydrogen at C-4 to yield the monodeuteriosemidione. The second hydrogen at C-4 exchanged much more slowly. The relative rates of exchange of the exo and endo hydrogen atoms were in the order 1:100 for the unsubstituted ketone and more like $1:10^3$–$1:10^5$ for the 6,6-dimethyl (**9**), *anti*-6-methyl (**10**), *anti*-6-ethyl (**12**), and 1-ethyl-5-methyl (**15**) derivatives. The tricyclic semidiones **33** showed a pronounced effect of ring size on the rate of exchange of the hydrogen at C-4. Thus, under comparable conditions, **33e** exchanged the α hydrogen in >1 min ($a_{4\text{-exo}}^{D}$ = 2.3 G), **33d** required 3 hr for complete exchange (a^D = 1.9G), and **33c** gave only partial exchange in 24 hr (a^D = 1.4 G). No exchange at any other point in the bicyclohexane nucleus was ever observed.

The intermediate involved in hydrogen exchange could be **43**, **44**, or **45**.[28] We feel that in anhydrous DMSO-d_6, the extremely stereoselective exchange noted



is most consistent with the radical dianion intermediate (**44**), formed by stereoselective exo attack at the C-4

(24) G. A. Russell and R. D. Stephens, *J. Phys. Chem.*, **70**, 1320 (1966). Spin residing on a hydrogen atom is $a^H/Q_H{}^H$ where Q^H is 500 for a free hydrogen atom but may be as large as 1000 for a hydrogen bonded to carbon.

(25) E. H. Stone and A. H. Maki, *J. Chem. Phys.*, **37**, 1326 (1962).

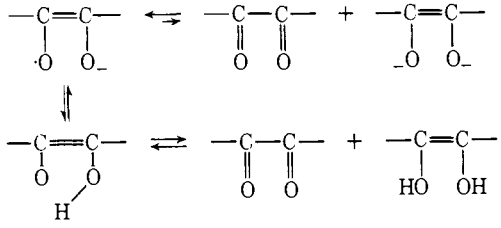
(26) H. C. Heller and H. M. McConnell, *J. Chem. Phys.*, **32**, 1535 (1960).

(27) D. I. Schuster and W. V. Curran, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, paper P 162.

(28) G. A. Russell and P. R. Whittle, *J. Amer. Chem. Soc.*, **91**, 2813 (1969).

methylene of **6**. By microscopic reversibility, reprotonation of **44** will also be expected to occur from the exo side. In solution containing D_2O the diketone may be an intermediate. The presence of D_2O decreases the lifetime of the semidione, perhaps by destruction of the unknown diketone by nucelophilic attack (Scheme X).

Scheme X



We have previously reported that in another bicyclic semidione base-catalyzed exchange was accelerated by the presence of deuterium oxide in the DMSO-d_6.[23] The addition of 2 vol % of D_2O to the DMSO-d_6 employed for exchange in the bicyclo[3.1.0]hexanesemidiones greatly accelerated the exchange for the parent system and for semidione **29**. Both methylene hydrogens in **6** were exchanged in 10 min (at least 20 hr was required in the absence of D_2O) and both methylene hydrogens in **29** in 2 hr (no two-deuterium exchange detected in **6** hr in the absence of D_2O). In the case of **29**, in the presence of D_2O the exchange was still stepwise (*i.e.*, 4-exo immediately exchanged, 4-endo took 2 hr for complete exchange).

The stereoselective exchange in the 4 position in the bicyclo[3.1.0]hexane nucleus could be due to a steric effect, such as the torsional effect discussed by Schleyer in the bicyclo[2.2.1]heptanones,[29] or a conjugative effect as discussed by Radlick and Rosen to explain the exclusive exo exchange in tricyclo[4.3.1.0]-deca-2,4,7-triene.[30] In **43–45** eclipsing of the hydrogens at C-4 and C-5 is relieved by exo attack on a proton and increased by endo attack.

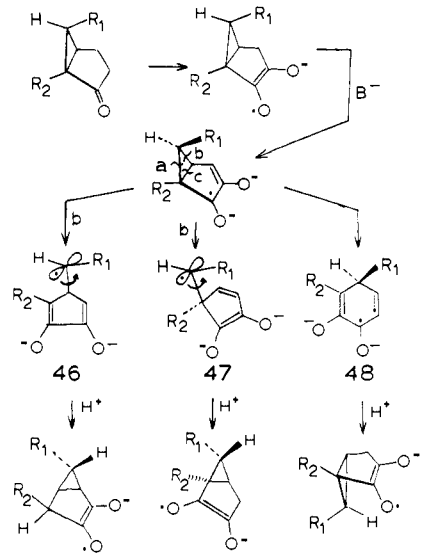
Molecular models would suggest that the five-membered ring of **6** or of **43–45** would be planar and would bisect the angle of the methylene group at C-4. However, the grossly different value of a^H for the exo and endo hydrogen atoms at C-4 *might* suggest that the exo C–H bond is much more nearly eclipsed with the π system.[31]

Rearrangement of Syn–Anti Substituted Bicyclo[3.1.0]hexanesemidiones. *syn*-6-Deuteriobicyclo[3.1.0]-hexanesemidione gave no indication of rearranging to the anti isomer. It was stable in DMSO solutions with little decrease in concentration for hours. On the other hand the *syn*-6-methyl or *syn*-6-ethyl derivatives readily isomerized to the anti derivatives and with a considerable decrease in the concentration of total paramagnetic species. This isomerization occurred much more rapidly in the presence of excess base and more rapidly when cesium *tert*-butoxide was used as the base than when potassium *tert*-butoxide was used.

The oxidation of *syn*-6-(methoxymethyl)bicyclo-[3.1.0]hexan-3-one in DMSO in the presence of potassium *tert*-butoxide produced initially a mixture of radicals. Upon standing, a spectrum consistent with the *anti*-6-(methoxymethyl) compound was formed. With cesium *tert*-butoxide as the base this spectrum was the initial one observed. Qualitatively the relative rates of isomerization of the syn-6 substituted semidione to its anti-6 isomer follows the sequence, $CH_3OCH_2 > C_2H_5 > CH_3 >>> D$. The rearrangement obviously involves a steric driving force from the relief of nonbonded interactions present in the syn-6-substituted semidione.

Since in DMSO-d_6 there is no exchange of hydrogen for deuterium at C-6, the simple base epimerization mechanism at C-6 can be eliminated. Therefore, cyclopropyl carbon–carbon bond cleavage seems most reasonable and three such cleavages can be pictured, each involving a separate carbon–carbon bond. These are pictured in Scheme XI.

Scheme XI



Mechanism a is pictured as a concerted 1,3 shift through transition state **46** with a rotation around the (C-5)–(C-6) bond. This process, not allowed by orbital symmetry considerations (Figure 2), yields the anti isomer. Mechanism b involves the same kind of rotation about (C-1)–(C-6) and would yield the anti isomer without the 1,3-carbon shift *via* intermediate **47**. Mechanism c can be pictured as a symmetry-allowed disrotatory ring opening and closure through the monocyclic intermediate **48**.

To differentiate among these routes, the 1-deuterio-*syn*-6-ethyl ketone (R_1 = Et; R_2 = D) was synthesized. The deuterium atom in the 1 position in the starting ketone was exclusively at the 1 position in the *anti*-6-ethyl semidione, thus eliminating mechanism a.

Path c could also be considered to proceed in a concerted fashion without a monocyclic intermediate. Orbital symmetry considerations predict that the disrotatory ring opening and closure of path c is allowed. There are analogies for reaction c in the literature. Thus, a diradical mechanism has been proposed for

(29) P. von R. Schleyer, *J. Amer. Chem. Soc.*, 89, 702 (1967).
(30) P. Radlick and W. Rosen, *ibid.*, 89, 5308 (1967).
(31) The EH calculation made with a bisected geometry at C-4 predicts a great difference in a^H for the exo and endo hydrogens. The effect of the cyclopropane ring is to move a nodal surface of the extended MO above (endo) the plane of the five-membered ring and to cause the endo hydrogen at C-4 to approach the nodal surface. This would decrease the hyperconjugative interaction with the endo hydrogen in the radical anion **6**. In a similar fashion, the maximum conjugation in a developing enolate anion would be expected to occur when the exo carbon–hydrogen bond is ionized. Maximum overlap with a minimum movement would thus result from the abstraction of the exo proton.

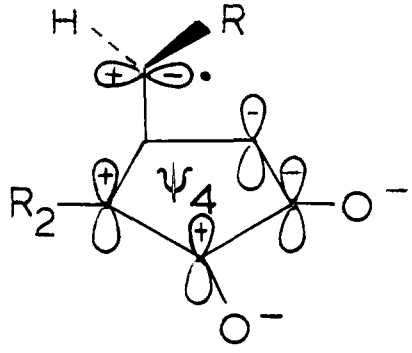


Figure 2. Orbital symmetries for transition state **46**: 2,3-dioxybutadiene, ψ_4, $\downarrow\downarrow$; ψ_3, $\uparrow\downarrow$; ψ_2, $\uparrow\downarrow$; ψ_1, $\uparrow\downarrow$; C-6 p orbital, $\uparrow$.

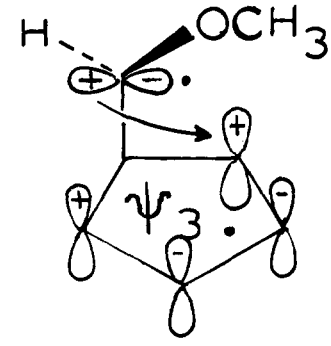
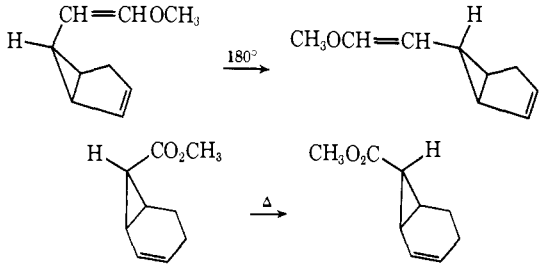


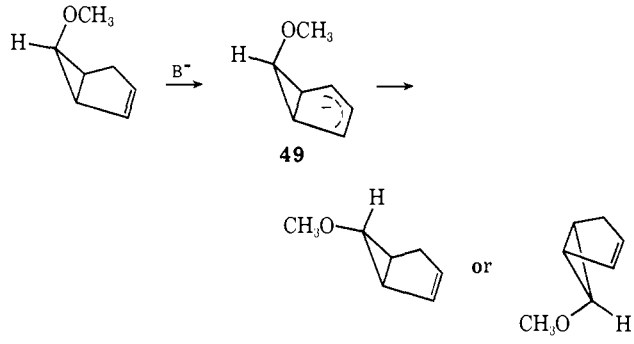
Figure 3. Orbital symmetries for 1,4-sigmatropic rearrangement of ion **49**: cyclopentadiene, ψ_3, $\uparrow$; ψ_2, $\uparrow\downarrow$; ψ_1, $\uparrow\downarrow$; C-6 p orbital, $\uparrow$.

thermal isomerizations in the bicyclo[3.1.0]hexene[32] and bicyclo[4.1.0]heptane[33] series (Scheme XII). Interesting, Schöllkopf and Paust report that *syn*-6-methoxybicyclo[3.1.0]hexane isomerizes to the trans isomer on basic aluminum but not on acidic alumina (Scheme XIII).[34] From the anion **49** a 1,4-sigmatropic rearrangement with retention of configuration at C-6 (which would lead to the *anti*-6-methoxy compound) is predicted (Figure 3).

Scheme XII



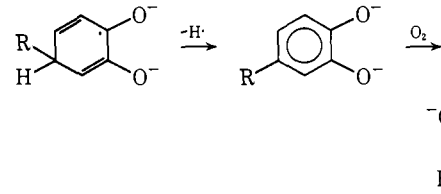
Scheme XIII



Both mechanisms b and c predict intermediates that could give side reactions resulting in the destruction of a large fraction of the paramagnetic centers. Moreover, the required steric driving force can be rationalized with both mechanisms because of the nonbonded interactions of the *syn*-6-alkyl group.

Further oxidation of a solution in which the rearrangement has proceeded to completion first destroys the esr signal of the *anti*-6-alkylbicyclo[3.1.0]hexanesemidione. Upon standing a new esr signal appears that can be identified as the 5-alkyl-4-hydroxy-*o*-benzosemiquinone (**50**). This semiquinone can be rationalized as being formed from the aromatized by-product of path c (Scheme XIV). The conversion of 4-alkyl-*o*-benzosemiquinones by base and oxygen to the 5-alkyl-4-hydroxysemiquinone has been documented by Waters.[35]

Scheme XIV



50, R = CH_3; a^H = 0.5, 0.8; $a_{CH_3}^H$ = 5.2; R = CH_3CH_2; a^H = 0.5, 0.8; $a_{CH_2}^H$ = 4.4

The semiquinone **50** is not formed by over-oxidation of *anti*-6-alkylbicyclo[3.1.0]hexan-2-ones in basic solution. Thus, it seems most likely that the rearrangement of *syn*- to *anti*-6-alkyl semidiones follows path c which produces by-products capable of oxidation to the 4-alkyl-*o*-semiquinones. Of course, one could imagine more complicated situations in which path b produced the syn–anti rearrangement and path c provided the by-product required for 4-alkyl-*o*-semiquinone formation.

In Figure 4 are given the esr spectra observed in the reactions of oxygen with *syn*-6-methylbicyclo[3.1.0]-hexan-2-one in DMSO solutions of potassium *tert*-butoxide. At the top is the unrearranged *syn*-6-methylbicyclo[3.1.0]hexane-2,3-semidione formed initially with a trace of oxygen. Upon standing a few hours, the spectrum in the middle of Figure 4 is formed. This spectrum is the initial one observed in the oxidation of *anti*-6-methylbicyclo[3.1.0]hexane. Upon addition of excess oxygen, this spectrum is destroyed and the one at the bottom of Figure 4 is formed. This *o*-semiquinone is also formed by oxidation of 4-methylcatechol.

Reaction of Bicyclo[3.1.0]hexanesemidiones with Excess Oxygen. Treatment of semidiones **6**, **10**, **12**, **18**, **19**, or **20** with excess oxygen resulted in the destruction of the semidione. Upon standing, a new esr signal was formed which was identified as an *o*-semiquinone. The structure of the semiquinone demanded that C-6 of the semidione had become C-3 in the semiquinone (Scheme XV).

(32) J. M. Brown, *Chem. Commun.*, 639 (1967).
(33) J. A. Berson and E. S. Hand, *J. Amer. Chem. Soc.*, 86, 1978 (1964).
(34) U. Schöllkopf and J. Paust, *Chem. Ber.*, 98, 2221 (1965).
(35) T. J. Stone and W. A. Waters, *J. Chem. Soc.*, 1488 (1965).

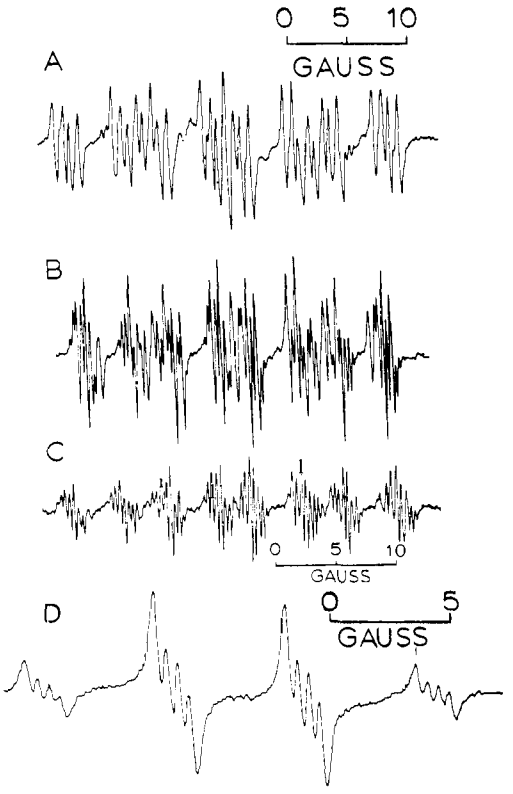
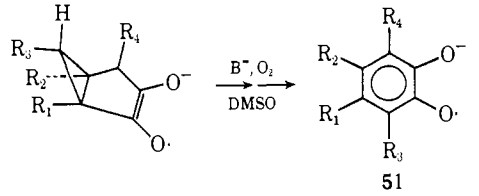


Figure 4. First-derivative esr spectra observed in the oxidation of *syn*-6-methylbicyclo[3.1.0]hexan-2-one (0.1 *M*) in the presence of potassium *tert*-butoxide (0.3 *M*) in DMSO solution: (A) initial spectrum of the *syn*-6-methyl semidione; (B) mixture of *syn*- and *anti*-6-methyl semidiones observed after 1.5 hr; (C) spectrum of the *anti*-6-methyl semidione observed after 3 hr; (D) the spectrum obtained by oxygenation of the solution yielding spectrum C. The spectrum is that of 5-methyl-4-hydroxy-*o*-benzosemiquinone. Similar results were obtained with the 6-ethylbicyclo[3.1.0]hexan-2-one except that under these reaction conditions the *syn*-semidione rearranged completely to the *trans*-semidione in 1 min or less.

Scheme XV



51

6, $R_1 = R_2 = R_3 = R_4 = H$; $a^H = 1.4, 1.4, 3.4, 3.4$
10, $R_1 = R_2 = R_4 = H$; $R_3 = CH_3$; $a^H = 1.0, 2.75, 3.6$; $a_{CH_3}^H = 1.0$
12, $R_1 = R_2 = R_4 = H$; $R_3 = CH_3CH_3$; $a^H = 1.0, 2.7, 3.5$; $a_{CH_2}^H = 1.0$
18, $R_1 = C_2H_5$; $R_2 = CH_3$; $R_3 = R_4 = H$; $a^H = 0.95, 0.95$; $a_{CH_3}^H = 3.4$; $a_{CH_2}^H = 3.9$
19, 20, $R_1 = i\text{-Pr}$; $R_2 = R_3 = H$; $R_4 = CH_3$; $a^H = 0.5, 3.0$; $a_{CH_3}^H = 0.6$; $a_{CH(CH_3)_2}^H = 2.9$

In Figures 5 and 6 the esr spectra observed in the oxidation of dihydroumbellulone are given. These spectra are identified as (Figure 5, top) the mainly unrearranged (4-*endo*-methyl) semidione (**19**) which upon standing (Figure 5, bottom) rearranges to mainly **20** (4-*exo*-methyl). Overoxidation produces 3-methyl-5-isopropyl-*o*-benzosemiquinone (Figure 6, top). Under the reaction conditions the oxidation of 2,5-dihydroxy-*p*-cymene or 2-hydroxythymoquinone produced **52**, Scheme XVI (Figure 6, bottom).

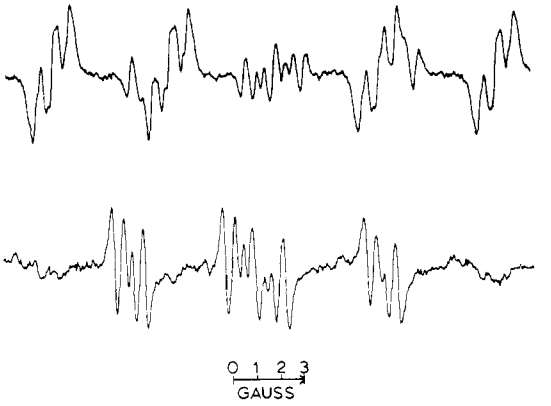


Figure 5. Oxidation products of 0.1 *M* β-dihydroumbellulone in DMSO containing 0.3 *M* potassium *tert*-butoxide: top, 20 min after oxidation, mainly **19**; bottom, after 6 hr, mainly **20**.

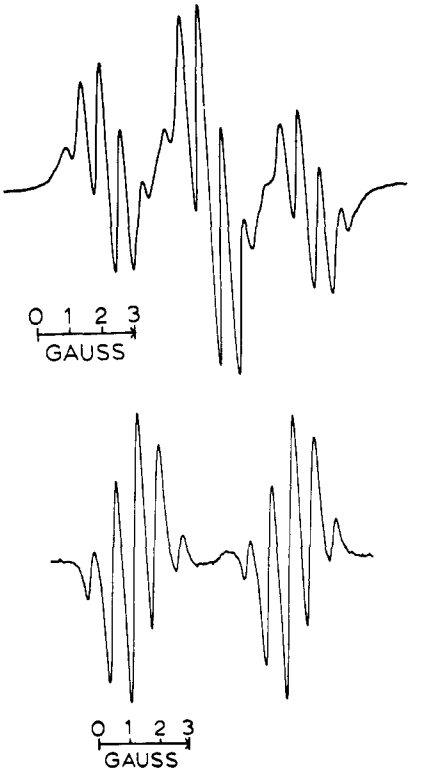


Figure 6. Top, semiquinone formed from overoxidation of semidiones derived from β-dihydroumbellulone or thujone in DMSO solution. The structure is assigned as 3-methyl-5-isopropyl-*o*-benzosemiquinone. Bottom, semiquinones formed upon oxidation of 2,3-dihydroxy-*p*-cymene or spontaneously from 2-hydroxythymoquinone in basic DMSO solution. Structure **52** is assigned.

In Figure 7 the conversion of *anti*-6-methylbicyclo-[3.1.0]hexan-2-one to the semidione and thence with excess oxygen to 3-methyl-*o*-benzosemiquinone is demonstrated.

A reasonable mechanism for the ring opening reaction would be the conversion of the semidione to the diketone by oxygen. Ionization to the enolate anion would provide an intermediate that could undergo a sigmatropic rearrangement of **53** to provide the cyclopropanol **54** which could undergo the normal cyclopropanol ring opening. Aromatization and oxidation would yield the semiquinone **51** (Scheme XVII). The orbital symmetries in the enolate anion are con-

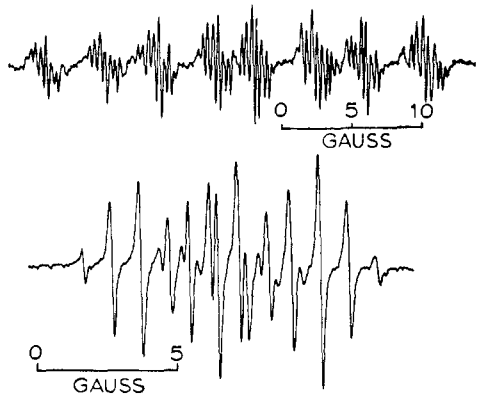
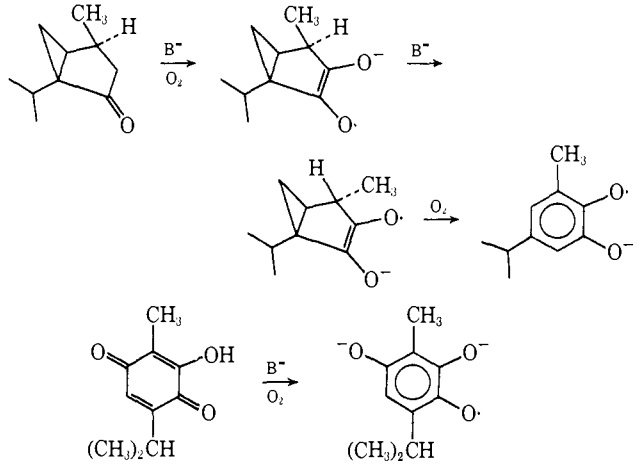


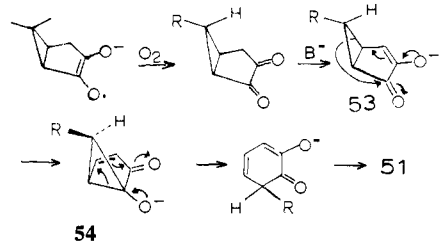
Figure 7. Oxidation products of *anti*-6-methylbicyclo[3.1.0]-hexan-2-one in DMSO in the presence of a threefold excess of potassium *tert*-butoxide: top, initial esr spectrum (**12**) stable for hours in the absence of excess oxygen; bottom, final oxidation spectrum formed after destruction of **12** with excess oxygen. The spectrum is that of **51** ($R_1 = R_2 = R_4 = H$; $R_3 = CH_3$).

Scheme XVI



52, $a^H = 0.7, 5.2$; $a_{CH_3}{}^H = 0.7$

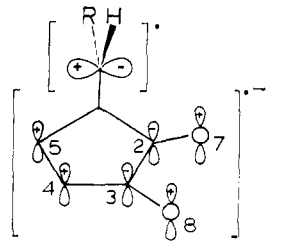
Scheme XVII



54

sistent with an inversion of configuration at C-6 in the formation of **54**. This would allow an anti substituent at C-6 to remain in the sterically favorable outside position during the conversion of **53** to **54**. Hückel calculations of the π system C-2–C-5, O-7, O-8 give the coefficients shown in Figure 8 for ψ_4. The sigmatropic rearrangement postulated to lead to the cyclopropanol derivative is similar to the slither mechanism reported by Zimmerman and coworkers in the photolysis of 4,4-diarylcyclohexadienones and in the dehydrobromination of 2-bromo-6,6-diarylbicyclo-[3.1.0]hexan-3-ones[36] or the debromination of 2,4-dibromo-6-phenyl-6-benzylbicyclo[3.1.0]hexan-3-one.[37]

(36) H. E. Zimmerman and D. S. Crumrine, *J. Amer. Chem. Soc.*, **90**, 5612 (1968); H. E. Zimmerman, D. S. Crumrine, D. Dopp, and P. S. Huyffer, *ibid.*, **91**, 434 (1969).

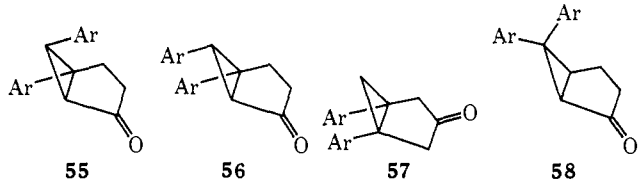


C-2 = -0.55 C-5 = +0.52
C-3 = -0.48 O-7 = +0.32
C-4 = +0.14 O 8 = +0.28

Figure 8. Orbital symmetries and Hückel coefficients of ψ_4 for the transition state leading to **54**.

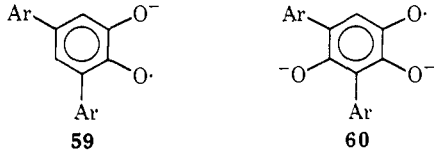
In the carbonium ion field a similar process occurs in the scrambling of the methyl groups in penta-, hexa-, and heptamethylbicyclo[3.1.0]hexenyl cation[38] and in the protonated form of hexamethylcyclopentenone.[39] These rearrangements all involve the formation of a new bond to an electron-deficient center in a 1,4-suprafacial manner and are analogous to the 1,3-suprafacial migration described by Berson and Nelson in the thermal conversion of bicyclo[3.2.0]hept-2-ene to bicyclo[2.2.1]heptene.[40]

The diphenylbicyclo[3.1.0]hexanes **55–58** were examined. Only semiquinones were detected from **55**, **56**, and **57**. The spectra were not completely resolved



55 **56** **57** **58**

but it appears that the same semiquinone is formed from all three starting ketones. Compound **55** gave initially a well-resolved spectrum with a^H = 2.1, 1.7, 1.7, 1.1, 1.1, 0.6, and 0.6 G which upon further oxidation yielded the same product as observed initially from **56**. The most reasonable interpretation seems to be that the semiquinones **59** and **60** are involved.



59 **60**

Compound **58** gave an esr signal with two large doublet splittings, a^H = 9.1 and 14.8 G. If this is due to the semidione, the geometry must be considerably different from that of the 6,6-dimethyl analog.

The aromatic ring apparently also favored ring opening in the oxidation of the tricyclic ketone **61**. The paramagnetic product has not been identified but the hfsc strongly suggest an aromatic semiquinone system.

(37) T. M. Brennan and R. K. Hill, *ibid.*, **90**, 5614 (1968).

(38) R. F. Childs and S. Winstein, *ibid.*, **90**, 7146 (1968); V. A. Koptyug, L. I. Kuzubova, I. S. Isaev, and U. I. Mantyuk, *Chem. Commun.*, 389 (1969).

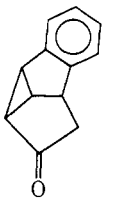
(39) D. W. Swatton and H. Hart, *J. Amer. Chem. Soc.*, **89**, 5075 (1967); H. Hart, T. R. Rogers, and J. Griffiths, *ibid.*, **91**, 754 (1969).

(40) J. A. Berson and C. L. Nelson, *ibid.*, **89**, 5503 (1967); J. A. Berson, *Accounts Chem. Res.*, **1**, 17 (1968).

Table II. Bicyclo[4.1.0]heptane-2,3-semidiones

Structure	a^H, G							
	1	4-cis	4-trans	5	6	7-syn	7-anti	Other
64	1.60	13.20	4.52	0.30	0.40	0.60	2.16	
65		13.30	4.80	0.40	0.40	0.40	2.60	
66	1.37	13.40[a]	4.45[b]			0.60	2.05	
67	1.18	13.38	4.17	0.38		0.76	2.18	0.20, 0.20
68		13.70	4.60	0.35		0.60	2.40	0.20[c]
69	5.18		0.65[c]	1.95		0.65	2.16	
70	5.10	7.60[e]	14.40[d]	0.80		0.1[c]	0.4[c]	

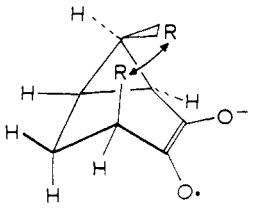
[a] a^D = 2.1 G. [b] a^D = 0.70 G. [c] $a_{CH_3}^H$. [d] a^D = 2.2 G. [e] a^D = 1.2 G.



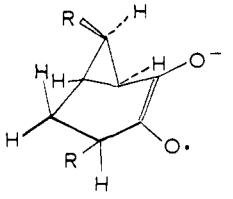
$\xrightarrow[DMSO]{B^-,O_2}$ a^H = 3.12, 2.70, 0.90, 0.78, 0.48 G

61

Bicyclo[4.1.0]heptane-2,3-semidiones. Dreiding models indicate two possible conformations **62** and **63** for bicyclo[4.1.0]heptane-2,3-semidiones. The conformational problem is similar to 2-carene that has been examined in pmr by Acharya.[41] In **62** there is a

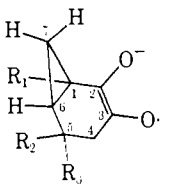


62

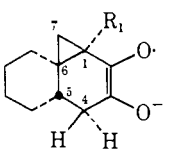


63

severe nonbonded interaction between the cis substituent at C-4 and the syn substituent at C-7. Substituents at these positions would be expected to favor conformation **63**. The dihedral angle made by the cyclopropyl methine hydrogen with the π system is much more favorable for interaction in **63** than in **62**, and thus a possible experimental distinction between preferred conformation can be made. The parent system apparently prefers conformation **62** since the α-cyclopropyl methine splitting is quite small. Semidiones **64–68** give a consistent interpretation in terms of the assignment of hfsc with conformation **62** (Table II). The hfsc of the 7-*anti*-hydrogen atoms in **64–68** have been assigned by analogy with the bicyclo[3.1.0]-hexane system.

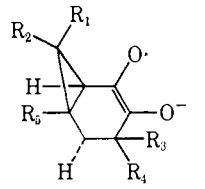


64, $R_1 = R_2 = R_3 = H$
65, $R_1 = CH_3$; $R_2 = R_3 = H$
66, $R_1 = H$; $R_2 = R_3 = CH_3$



67, $R_1 = H$
68, $R_1 = CH_3$

Substitution of methyl groups at C-4 or C-7 had a drastic effect on the hfsc of the remaining hydrogen atoms. We believe this reflects a change in preferred conformation from **62** or **63**. A consistent assignment of hfsc to the two derivatives (**69** and **70**) that we believe exist in conformation **63** is given in Table II.



exo

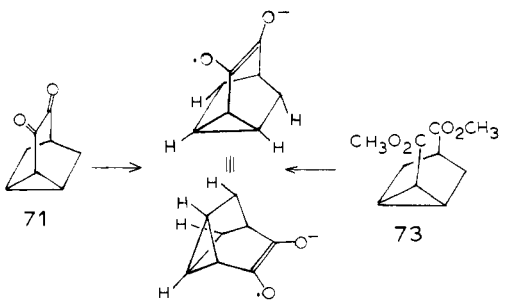
69, $R_1 = R_2 = H$; $R_3 = R_4 = R_5 = CH_3$
70, $R_1 = R_2 = CH_3$; $R_3 = R_4 = R_5 = H$

Compounds **66** and **70** underwent exchange of both α hydrogen atoms in DMSO-d_6. For **70** it was possible to observe first the exchange of the 14.40-G (exo) hydrogen and then the exchange of the 7.60-G (endo) hydrogen atom. In **66** both hydrogens exchanged rapidly and could not be differentiated. In **69** we note that the exo hydrogen at C-5 forms a very good W-plan arrangement with the p_z orbital at C-3 (as in bicyclo-[2.2.1]heptanesemidione) and a fairly significant doublet splitting is assigned to this position.

Oxidation of 6-methylbicyclo[4.1.0]heptan-2-one, 4,6-dimethylbicyclo[4.1.0]heptan-2-one, 7,11,11-trimethyltricyclo[5.5.0.0^{1,3}]undecan-4-one (dihydromayurone), or 7-methyltricyclo[5.4.0.0^{1,3}]undecan-4-one in basic DMSO solution failed to yield well-resolved esr signals.

One tricyclic derivative of bicyclo[4.1.0]heptane-2,3-semidione was examined. Diketone **71**[42] was reduced by the enolate anion of propiophenone to apparently yield **72**. Semidione **72** was one of several radicals formed from the acyloin condensation of diester **73**,[43] Scheme XVIII.

Scheme XVIII



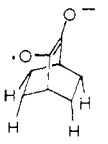
72, a^H = 0.55, 0.55, 0.22, 0.22 G

(41) S. P. Acharya, *Tetrahedron Lett.*, 4117 (1966); S. P. Acharya and H. C. Brown, *J. Amer. Chem. Soc.*, 89, 1925 (1967).

(42) Prepared by selenium dioxide oxidation of the mono ketone reported by J. T. Lumb and G. H. Whitham, *Tetrahedron*, 21, 499 (1965).

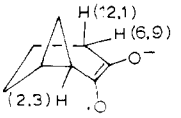
(43) Prepared by oxidation of the olefin reported by C. A. Grob and J. Hosthnck, *Helv. Chem. Acta*, 46, 1676 (1963).

The hyperfine splitting constants of **72** are somewhat surprising in view of the assignments for **64** and for **74**.[21]



74, a^H = 2.1, 2.1, 2.1, 2.1 G

Bicyclo[5.1.0]octane-2,3-semidione. Oxidation of bicyclo[5.1.0]octan-2-one gave a semidione in which the main splittings were a^H = 12.1, 6.9, 2.3 G. In DMSO-d_6 the 12.1- and 6.9-G splittings were replaced by a_D = 1.9, 1.0. It seems that the most likely conformation and assignment of hfsc are as shown in structure **75** wherein the α-cyclopropyl methine hydrogen is close to the nodal plane of the π system. The W-plan arrangement between the anti position at C-8 and the p_z orbital at C-2 is now rather poor.



75, a^H = 0.3, 0.3, 0.3 unassigned

Bicyclo[6.1.0]nonane-2,3-semidione. Oxidation of bicyclo[6.1.0]nonan-2-one gave a semidione with a^H = 12.5, 6.0, 1.7, 1.0, and 0.2 G. In DMSO-d_6 the hydrogens with a^H = 12.5 and 6.0 G were replaced with deuterium identifying these hydrogens as the α-methylene group. The 1.0- or 1.7-G hydrogen is probably at the cyclopropyl methine position. The geometry around the semidione is very similar to that in the bicyclo[5.1.0]octanesemidione.

Experimental Section

Molecular Orbital Calculations. The molecular orbitals (ψ_u) were formed as linear combinations of orthogonal atomic orbitals (ϕ_{ui}) normalized according to eq 2.[44] The group overlap integrals

$$\psi_u = \sum_i c_{ui}\phi_{ui} \tag{1}$$

$$\sum_i c_{ui}^2 + \sum_{i\neq j} c_{ui}c_{uj}S_{ij} = 1 \tag{2}$$

are represented by S_{ij}. The overlap matrix was calculated using a basis set of Slater-type orbitals (eq 3) by the method of Hoffmann and Lipscomb.[45] In eq 3, N is the normalization factor, n, l,

$$\phi(n,l,m,z) = Nr^{n-1}\exp(-zr)Y^m(\theta,E) \tag{3}$$

and m are quantum numbers, z is the orbital exponent, Y is the spherical harmonic, and r, θ, and E are the respective polar coordinates. The orbital exponents used were obtained by Cusachs' eq 4 where values of $\langle r\rangle$ have been calculated from the many-

$$z = \frac{n + 0.5}{\langle r\rangle} \tag{4}$$

term SCF functions.[12,46] The diagonal elements of the Hamiltonian matrix were calculated using the method of Cusachs'[12] eq 5 where H_{ii}° is the valence state ionization potential, AQ_i the charge transfer correction term, and BQ_b the neighbor atom potential correction term. The term Q_i is the net charge on atom i

$$H_{ii} = H_{ii}^\circ - AQ_i - BQ_b^* \tag{5}$$

(44) R. S. Drago and H. Petersen, Jr., *J. Amer. Chem. Soc.*, 89, 3978 (1967).
(45) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, 36, 2179 (1962).
(46) E. Clementi, *ibid.*, 38, 996, 1001 (1963); 41, 295, 303 (1964); C. Froese, *ibid.*, 45, 1417 (1966).

Table III. Input Parameters for EH-SCF Calculations

Orbital	H_{ii}°	A	B	z	n
C_{2s}	−19.5	11.9	14.7	1.57	2
C_{2p}	−11.2	11.9	14.7	1.46	2
O_{2s}	−33.2	15.2	18.8	2.19	2
O_{2p}	−16.1	15.2	18.8	2.03	2
K_{4s}[a]	−2.7	4.0	2.1	0.44	3
H_{1s}	−13.6	0	0	1.20	1

[a] Inclusion of the K_{4p} orbitals had little effect on the calculations.

and Q_b^* is the neighbor atom "effective charge term." Values of A, B, and z are given in Table III.

For optimum convergence a damping factor D had to be included. All changes in the net charges of the atoms, and the Q_b^* terms, were damped by use of eq 6 and 7 where I corresponds to the input and II the output of the previous calculation. Values of D of 2.5–3.0 were used and six–eight iterations were generally required for convergence to self-consistent charges of within 0.02 unit.

$$Q_i(\mathrm{I}) = \frac{DQ_i(\mathrm{I}) + Q_i(\mathrm{II})}{1 + D} \tag{6}$$

$$Q_b^*(\mathrm{I}) = \frac{(D - 0.5)Q_b^*(\mathrm{I}) + Q_b^*(\mathrm{II})}{0.5 + D} \tag{7}$$

The off-diagonal elements were obtained from the overlap matrix by eq 8, where S_{ij} are the group overlap integrals and $|S_{ij}|$ are the

$$H_{ij} = S_{ij}(2 - |S_{ij}|)(H_{ii}H_{jj})^{1/2} \tag{8}$$

atomic overlap integrals. The $S_{ij}(2 - |S_{ij}|)$ terms are computed in the local coordinate system prior to rotation to the molecular coordinate systems. The use of the geometric mean of H_{ii} and H_{jj} is the modification that Ballhausen and Gray[47] applied to the Wolfsberg and Helmholz formula.[48]

The first-order Fermi contact term is evaluated as $a^H = 878c_{ui}^2$ G.[11,44] We used $a^H = 790c_{ui}^2$ G in evaluating hydrogen hyperfine splitting constants. In most cases Σc_{ui}^2 was approximately 1.11 and hence a reduction of 10% in the scaling factor was used. The use of the ψ^2 routine of Drago and Petersen[44] wherein the value of Σc_{ui}^2 was estimated at each hydrogen nucleus did not give as good agreement with the experimental as simply estimating c_{ui}^2 for atom i. The presence of the potassium cation had a significant effect on the calculated spin densities for bicyclo[3.1.0]hexanesemidione.

Esr Spectra. Details on the preparation of semidiones from ketones, α-hydroxy ketones, or diketones in DMSO solution in the presence of potassium *tert*-butoxide have been given previously.[49] An inverted U-type mixing cell was used for all experiments. Spectra were recorded on a Varian Associates E-3 spectrometer in a flat fused silica cell (Varian aqueous sample cell). Spectra were simulated with a Japan Electron Optics Laboratory Co., JNM-RA-1 spectrum accumulator by the superposition of a series of Lorentzian line shapes. Line widths were generally 0.1 G or less.

Reagents. **Bicyclo[3.1.0]hexan-3-one** was prepared according to the literature.[50] The 2,4-dinitrophenylhydrazone had mp 149–150°, lit.[50] 149.2–149.8°.

Bicyclo[3.1.0]hexan-2-one was prepared by the reaction of dimethylsulfonium methylide with 2-cyclopentenone. The ylide was prepared from 0.5 g of sodium hydride and 4.62 g of trimethylsulfoxonium iodide in 25 ml of DMSO at 25°. Fifteen minutes after preparation of the ylide, 1.62 g of the ketone in 5 ml of DMSO was added with vigorous stirring. The mixture was stirred 2 hr at 25° and 1 hr at 50° before being treated with 80 ml of water following by ethereal extraction. The ether extract was dried (Na_2SO_4) and distilled to give 1.1 g (65%) of the ketone, bp 55° at 10 Torr; 2,4-dinitrophenylhydrazone, mp 169–171°, lit.[51] mp 170–172°.

syn-**6-Deuteriobicyclo[3.1.0]hexan-3-one** was prepared from *syn*-6-deuterio-*cis*-bicyclo[3.1.0]hexane-3-carboxylic acid.[52] The acid

(47) C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, 1, 111 (1962).
(48) M. Wolfsberg and L. Helmholz, *J. Chem. Phys.*, 20, 837 (1952).
(49) E. R. Talaty and G. A. Russell, *J Amer. Chem. Soc.*, 87, 4867 (1965).
(50) S. Winstein and J. Sonnenberg, *ibid.*, 83, 3235 (1961).
(51) N. A. Nelson and G. A. Mortimer, *J. Org. Chem.*, 22, 1146 (1957).

(4.2 g, 0.032 mol) was treated with 0.18 mol of methyllithium. Distillation yielded 3.2 g of the methyl ketone, bp 71–72° at 10 Torr, lit.[52] bp 78° at 16 Torr. The ketone was treated with excess methylmagnesium bromide and the resulting alcohol dehydrated with phosphorus oxychloride in pyridine solution.[53] The crude olefin was ozonized at 0° in CCl_4.[54] The ketone was isolated by preparative glpc (20% SF-96 on firebrick; column temperature 150°) and had an identical retention time with the undeuterated ketone: ir (neat) 3050 (cyclopropyl C–H), 2240 (cyclopropyl C–D), 1740 cm^{-1} (C=O); pmr (CCl_4) δ 0.8 (t, 1, J = 8 Hz, *anti*-6-cyclopropyl hydrogen[55]), 1.52.6 (m, 6). The syn-6 proton at δ 0.1 was absent. The mass spectrum (70 eV) gave parent ions at *m/e* 97.

6,6-Dideuteriobicyclo[3.1.0]hexan-2-one was prepared from Δ^2 cyclopentenol[56] and the Simmons–Smith reagent from dideuteriomethylene iodide.[57] The procedure was identical with that used to prepare bicyclo[3.1.0]hexan-3-one from Δ^3-cyclopentenol and methylene iodide.[50] The pure ketone was isolated by glpc (20% SF-96 on firebrick; column temperature 150°): ir (CCl_4) 2400 (cyclopropyl C–D), 1725 cm^{-1} (C=O); pmr (CCl_4) δ 1.5–2.1 (m); mass spectrum (70 eV) *m/e* (relative intensity) 98 (100), 97 (14).

***anti*-6-Methylbicyclo[3.1.0]hexan-2-one** was prepared from *trans*-*n*-hex-4-enoic acid[58] by the procedure of Fawzi and Gutche.[15] The acid (*p*-bromophenacyl ester, mp 82–83°; lit.[53] mp 82°) was converted to the acid chloride (not isolated), diazo ketone (not isolated), and to the bicyclo[3.1.0]hexan-2-one, bp 74–76° at 8 Torr, in an overall yield of 30%: ir (neat) 3050 (cyclopropyl CH), 1710 cm^{-1} (C=O); pmr (CCl_4) δ 1.15–2.2 (m, 6), 1.1 (s, 3, CH_3), 1.0 (s, 1, syn-6 proton); mass spectrum (70 eV) *m/e* at 116 (parent ions). The 2,4-dinitrophenylhydrazone had mp 118–120°.

Anal. Calcd for $C_{13}H_{14}NO_2$: C, 53.79; H, 4.83. Found: C, 53.71; H, 4.80.

***syn*-6-Methylbicyclo[3.1.0]hexan-2-one** was prepared from *cis*-*n*-hex-4-enoic acid[58] by the method of Fawzi and Gutche[15] in an overall 30% yield. The acid gave a *p*-bromophenacyl ester, mp 54–55°, lit.[58] mp 55°. The final ketone, bp 60–62° at 4 Torr, had a 3-min shorter retention time from the anti isomer in glpc (20% SF-96 on firebrick; column temperature 150°): ir (neat) 3050 (cyclopropyl CH), 1718 cm^{-1} (C=O); pmr (CCl_4) δ 1.0–2.2 (m); mass spectrum (70 eV) *m/e* 110 (parent ion). The 2,4-dinitrophenylhydrazone had mp 124–127°.

Anal. Calcd for $C_{13}H_{14}N_4O_4$: C, 53.79; H, 4.83. Found: C, 53.64; H, 4.77.

1-Methylbicyclo[3.1.0]hexan-2-one was prepared from 1-methylcyclopentene *via* nitrosyl chloride addition and hydrolysis[59] to 2-methyl-2-cyclopentone which could be converted by the dimethylsulfonium methylide reagent to the desired ketone. To 25 g of 1-methylcyclopentene in ether at −30°, nitrosyl chloride was added until the solution became brown. The white precipitate was filtered and hydrolyzed in 1 l. of 2% sulfuric acid for 4 hr. The aqueous solution was steam distilled and the distillate extracted with three 100-ml portions of ether. The ether was dried (Na_2SO_4) and distilled to give 3.0 g of 2-methyl-2-cyclopentenone (10%), bp 48° at 14 Torr. The bicyclohexanone was isolated by glpc (20% SF-96 on firebrick; column temperature 150°): ir (neat) 3050 (cyclopropyl CH), 1710 cm^{-1} (C=O); pmr (CCl_4) δ 1.7–2.0 (m, 5), 1.2 (s, 3, CH_3), <1 (m, 2); mass spectrum (70 eV) *m/e* 110 (parent ion). The ketone gave a 2,4-dinitrophenylhydrazone, mp 182–184°, lit.[60] mp 186–187°.

Anal. Calcd for $C_{13}H_{14}N_4O_4$: C, 53.79; H, 4.83. Found: C, 53.68; H, 4.81.

5-Methylbicyclo[3.1.0]hexan-2-one was prepared from 3-methyl-2-cyclopenten-1-one[61] *via* the alcohol and methylene iodide in the presence of a zinc–copper couple.[62] Reduction of 5-methyl-2-cyclopenten-1-one with lithium aluminum hydride gave the alcohol, bp 77–78°, at 30 Torr. A mixture of 0.32 mol of the zinc–copper couple, 58 g of methylene iodide, and 0.1 g of iodine in 250 ml of ether was refluxed gently for 30 min. The 3-methyl-2-cyclopenten-1-ol (8.5 g, 0.088 mol) in 40 ml of ether was added during 45 min. After stirring under reflux for 24 hr, 35 ml of saturated aqueous NH_4Cl solution was added. The precipitated salts were washed with ether and the combined ethereal extracts washed with saturated aqueous NaCl and dried ($MgSO_4$). After removal of the ether under vacuum the residue was added to 50 ml of a saturated solution of sodium methoxide in methanol and the mixture allowed to stand overnight. The mixture was dissolved in ether and extracted with saturated aqueous NaCl until the aqueous extract was neutral. The ethereal solution was dried ($MgSO_4$) and rectified to yield 4.3 g (43%) of the 5-methylbicyclo[3.1.0]hexan-2-ol. The alcohol was oxidized with 12 g of chromium trioxide in 125 ml of pyridine for 12 hr at 25°. Work-up[63] gave the ketone, bp 90–94° at 45 Torr, which was purified by glpc (20% SF-96 on firebrick, 150°): ir (CCl_4) 3060, 1020 (cyclopropyl), 1721 cm^{-1} (C=O); pmr (CCl_4) δ 2.10 (m, 1), 1.98 (t, 3, J = 1.5 Hz), 1.48 (m, 1), 1.32 (s, 3), 1.10 (s, 1), 1.04 (t, 1, J = 2.5 Hz); mass spectrum (70 eV) *m/e* 110 (parent ion). The semicarbazone had mp 148.5–149.5° and the 2,4-dinitrophenylhydrazone mp 138–140°, lit.[54] mp 138–139°.

6,6-Dimethylbicyclo[3.1.0]hexan-2-one was prepared by the photolysis of 4,4-dimethyl-2-cyclohexenone in 600 ml of *tert*-butyl alcohol with a high-pressure mercury lamp for 48 hr.[64] Distillation of the *tert*-butyl alcohol left an oil that was purified by glpc (5% LAC-446 on Chromosorb P; column temperature 140°) to give material identical with that described previously.[64]

***anti*-6-Ethylbicyclo[3.1.0]hexan-2-one** was synthesized by the ring closure technique of Fawzi and Gutche from *trans*-*n*-hept-3-enoic acid. *trans*-*n*-Hex-3-en-1-ol[65] was converted to the heptenoic acid by conversion to the bromide followed by carbonation of the Grignard reagent. The technique followed exactly that used previously in the chain extension of *cis*-*n*-pent-3-en-1-ol to *cis*-*n*-hex-3-enoic acid.[58] The *trans*-*n*-hept-3-enoic acid, bp 81° at 0.75 Torr, *p*-bromophenacyl ester, mp 78.5–79.5°, was converted to the acid chloride (not isolated), diazo ketone (not isolated), and thence to *anti*-6-ethylbicyclo[3.1.0]hexan-2-one, bp 60° at 36 Torr: ir (neat) 3050 (cyclopropyl CH), 1712 cm^{-1} (C=O); pmr (CCl_4) δ 1.0–2.2; mass spectrum (70 eV) *m/e* 124 (parent ions). The 2,4-dinitrophenylhydrazone had mp 136–138°.

Anal. Calcd for $C_{14}H_{16}N_4O_4$: C, 55.29; H, 5.26. Found: C, 55.21; H, 5.21.

***syn*-6-Ethylbicyclo[3.1.0]hexan-2-one** was synthesized from commercial *cis*-*n*-hex-3-en-1-ol (Aldrich Chemical Co.) by conversion to *cis*-*n*-hept-3-enoic acid by the standard procedure.[58] The *cis*-*n*-hept-3-enoic acid, bp 85° at 1.5 Torr, *p*-bromophenacyl ester, mp 50.5–51.5°, was converted to the acid chloride (not isolated), diazo ketone (not isolated), and hence to the bicyclic ketone. The bicyclic ketone had a 2.5-min shorter glpc retention (20% SF-96 on firebrick; column temperature 150°) from the anti isomer. *syn*-6-Ethylbicyclo[3.1.0]hexan-2-one had bp 65° at 4 Torr: ir (neat) 3050 (cyclopropyl CH), 1720 cm^{-1} (C=O); pmr (CCl_4) δ 1.0–2.3; mass spectrum (70 eV) *m/e* 124 (parent ion). The 2,4-dinitrophenylhydrazone had mp 113–114°.

Anal. Calcd for $C_{14}H_{16}N_4O_4$: C, 55.29; H, 5.26. Found: C, 55.23; H, 5.24.

1-Deuterio-*syn*-6-ethylbicyclo[3.1.0]hexan-2-one was synthesized from *cis*-*n*-hept-3-enoic acid chloride and diazomethane-d_2. Partially deuterated diazomethane was generated from Diazald, deuterium oxide, Carbitol, and potassium hydroxide by normal techniques.[66] To an ice-cold ethereal solution of partially deuterated diazomethane was added 50 ml of deuterium oxide containing 1 g of potassium carbonate. The two phase solution was stirred for 45 min. The aqueous layer was removed and replaced by more deuterium oxide and potassium carbonate. After again removing the aqueous layer, the ethereal diazomethane-d_2 was distilled, employing the usual precautions.[66] This procedure provided diazomethane-d_2 with greater than 97% deuterium incorporation. *cis*-*n*-Hept-3-enoic acid was then converted[15] to the 1-deuterio-*syn*-6-ethylbicyclo[3.1.0]hexan-2-one in 35% yield, bp 65° at 4 Torr. The glpc (20% SF-96 on firebrick; column temperature 150°) retention time was identical with that of the undeuterated cis isomer: ir

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(neat) 3050 (cyclopropyl CH), 2273 (cyclopropyl CD), 1715 cm^{-1} (C=O); pmr (CCl_4) δ 0.8–2.0; mass spectrum (70 eV) *m/e* 125 (parent ion).

syn-6-(**Methoxymethyl**)**bicyclo[3.1.0]hexan-3-one** was prepared from *syn*-bicyclo[3.1.0]hex-2-ene-6-carboxyladehyde.[67] The aldehyde was reduced by LAH to the alcohol, bp 77–79 at 9 Torr.[66] The alcohol (9.5 g, 0.086 mol) was added to 6.5 g (0.27 mol) of NaH in 300 ml of ether. After stirring for 2 hr, 45 g of methyl iodide was added and the solution stirred for 69 hr under nitrogen. The excess NaH was destroyed by methanol and saturated aqueous ammonium chloride was added until the inorganic salts precipitated. The dried ethereal solution was distilled to yield 8.8 g (83% of *syn*-6-(methoxymethyl)bicyclo[3.1.0]hexene, bp 76–78° at 47 Torr. To 8.7 g of the unsaturated ether in 15 ml of diglyme was added 0.92 g of sodium borohydride in 25 ml of diglyme followed by the addition of 4.3 g of boron trifluoride ethereate in 10 ml of diglyme over a period of 1 hr at 5°. After stirring for 1 hr, 6 ml of water and 10 ml of 3 *M* aqueous sodium hydroxide were added followed by the addition of 10 ml of 30% hydrogen peroxide over a period of 1.5 hr. The solution was diluted with 50 ml of water and extracted with ether. The dried ($MgSO_4$) ether extract was distilled to give 3.6 g (36%) of the alcohol, bp 91–94° at 2 Torr. A solution of 3 g of the alcohol in 10 ml of pyridine was added to 6 g of chromium trioxide in 70 ml of pyridine. After stirring for 11 hr, 1.2 g of the ketone was obtained: bp 84–86° at 5 Torr; ir (CCl_4) 3050 (cyclopropyl CH), 1740 (C=O), 2800, 1144 cm^{-1} (OCH_3); pmr (CCl_4) δ 1.10–1.95 (m, 3), 2.20–2.80 (m, 4), 3.18 (d, 2, J = 7 Hz), 3.25 (s, 3). The 2,4-dinitrophenylhydrazone had mp 149–150°.

Anal. Calcd for $C_{14}H_{16}N_4O_5$: C, 52.52; H, 5.00; N, 17.50. Found: C, 52.38; H, 5.30; N, 17.29.

Sabina ketone (**5-isopropylbicyclo[3.1.0]hexan-2-one**) was prepared from 4.8 g of sabinene (Fluka AG) by oxidation with 12 g of $KMnO_4$ and 3 g of NaOH in 80 ml of water and 80 g of ice. The mixture was shaken for 1 hr after which time the manganese dioxide was filtered and washed with water. The filtrates were concentrated to 20 ml and the residue (3.6 g) was removed by filtration. The residue was dissolved in 35 ml of hot water containing 1.5 ml of 10% sulfuric acid. A solution of 2.2 g of $KMnO_4$ and 1.5 ml of concentrated sulfuric acid in 60 ml of water was added dropwise while passing a current of steam through the system. The distillate (50 ml) was saturated with NaCl and thoroughly extracted with ether. Evaporation of the ether left 300 mg of an oil from which sabina ketone was isolated by glpc (20% SF-96 on firebrick at 165°): ir (CCl_4)[69] 3050, 1722, 1383, 1364, 1019 cm^{-1}; pmr (CCl_4) δ 1.85–2.30 (m, 4), 1.38–1.80 (m, 2), 0.97–1.20 (m, 8); semicarbazone, mp 135–136° (lit.[70] mp 135–137°).

1-Ethyl-5-methylbicyclo[3.1.0]hexan-2-one was prepared from 2-ethyl-3-methyl-2-cyclopentenone.[71] γ-Methyl-γ-propylbutyrolactone[72] was placed in 100 ml of commercial polyphosphoric acid and heated to 100° for 2 hr. The solution was poured onto ice and extracted with ether. The ether was washed with aqueous sodium chloride and dried over Na_2SO_4. Distillation yielded 13 g (87%) of 2-ethyl-3-methylcyclopentenone, bp 95–96° at 18 Torr, lit.[71] bp 95–96° at 18 Torr. Reduction of the ketone with LAH in ether gave 2-methyl-3-ethyl-2-cyclopenten-1-ol, bp 76° at 6 Torr. Methylene insertion was performed as in the case of 3-methylcyclopent-2-en-1-ol to give 55% 1-ethyl-5-methylbicyclo[3.1.0]hexan-2-ol, bp 83–84° at 10 Torr. Oxidation of the alcohol with chromium trioxide in pyridine gave the ketone that was purified by glpc (20% SF-96 on firebrick; column temperature 150°): ir (neat) 3050 (cyclopropyl CH), 1710 cm^{-1} (C=O); pmr (CCl_4) δ 1.3 (s, 3), 0.6–2.0 (m, 11); mass spectrum (70 eV) *m/e* 138 (parent ion). The 2,4-dinitrophenylhydrazone had mp 164–166°.

Anal. Calcd for $C_{15}H_{18}N_4O_4$: C, 56.60; H, 5.66. Found: C, 56.51; H, 5.56.

Thujone (**2-methyl-5-isopropylbicyclo[3.1.0]hexan-3-one**) was obtained as a mixture of α and β isomers from Fluka AG. The material was purified by vacuum distillation, bp 65–66° at 7 Torr, and preparative glpc (20% SF-96 on firebrick, 1/4 in. × 6 ft, 160°).

Dimethyl homothujadicarboxylate was prepared from 4-hydroxymethylenethujone, bp 89–91° at 3 Torr (lit.[73] bp 115–118° at 16 Torr). To a solution of 1 g of the hydroxymethylene ketone in a mixture of 100 ml of 10% aqueous NaOH and 65 ml of methanol there was added 25 ml of 30% hydrogen peroxide over 20 min. After stirring for 17 hr, the solution was cooled to 5° and acidified with cold 50% aqueous sulfuric acid. The solution was diluted to 750 ml with water, saturated with NaCl, and extracted with three 50-ml portions of ether. The ether extracts were washed with 10% aqueous NaOH (three 70-ml portions) and the basic extracts again acidified with 50% sulfuric acid. After saturation with NaCl the aqueous solution was extracted with ether. The ethereal extract was dried ($MgSO_4$) and concentrated to give 1 g of a viscous oil which was dissolved in 50 ml of ether. A distilled diazomethane solution (in 100 ml of ether) from 7 g of Diazald was added. After 18 hr the excess diazomethane was treated with acetic acid. The ethereal solution was washed with saturated aqueous $NaHCO_3$ (three 30-ml portions) followed by saturated aqueous NaCl. After drying ($MgSO_4$) the ether was removed under vacuum to yield 1.2 g of crude dimethyl homothujadicarboxylate[74] that was purified by glpc (15% Carbowax 20 M on Chromosorb W at 170°): ir (CCl_4) 1725, 1735 cm^{-1} (C=O); pmr (CCl_4) δ 0.65–1.28 (m, 13), 2.24 (q, 1, J = 7 Hz), 3.57 (s, 3), 3.60 (s, 3); mass spectrum (70 eV) *m/e* 228, 213, 197, 181, 169.

2,2-Dimethyl-5-isopropyl-4-*n*-butylthiomethylenebicyclo[3.1.0]hexan-3-one was prepared from hydroxymethylenethujone.[73] To 5.2 g (0.029 mol) of the ketone in 50 ml of benzene was added 3.0 g (0.033 mol) of *n*-butyl mercaptan and 15 mg of *p*-toluenesulfonic acid.[10] The resulting solution was refluxed for 11 hr with separation of water in a Dean-Stark trap. The solution was washed with 10% aqueous $NaHCO_3$ and with water. After drying ($MgSO_4$), vacuum distillation gave 5.0 g (69%) of the *n*-butylthiomethylene ketone, bp 111–119° at 0.25 Torr. The thio enol ether (4.5 g) was added to a solution of 3.5 g of potassium in 100 ml of *tert*-butyl alcohol and at 0° methyl iodide (8 ml) was added. The solution was refluxed for 2 hr and concentrated to about 10 ml. The residue was added to 40 ml of water which was then thoroughly extracted with water. The ether solution was dried ($MgSO_4$) and concentrated to give 2.4 g of a viscous oil purified by chromatography on alumina to yield a solid recrystallized from methanol: mp 130–132°; ir (CCl_4) 3060, 1036 (cyclopropyl), 1720 (C=O), 1618 (C=C), 1116, 1082 (=C—S—C); pmr (CCl_4) δ 0.22 (s, 1), 0.60–2.30 (m, 22), 2.50–3.10 (m, 2), 7.27 (s, 1); mass spectrum (70 eV) *m/e* 266 (parent ion).

6,6-Diphenylbicyclo[3.1.0]hexan-2-one was prepared by the method of Zimmerman and Swenton,[75] mp 87.5–89.0° from hexane; 2,4-dinitrophenylhydrazone, mp 154–156°. *cis*- **and** *trans*-**5,6-Diphenylbicyclo[3.1.0]hexan-2-one** were prepared and purified according to Zimmerman and Hancock.[76] **1,5-Diphenylbicyclo[3.1.0]hexan-3-one** was prepared by the procedure of Corey and Uda.[77]

2-Hydroxythymoquinone was prepared by the oxidation of β-dihydroumbellulone with selenium dioxide.[78] **4-Methyl-5-ethylcatechol** was prepared from 4-methylveratrole (50 g, 0.33 mol) which was dissolved in carbon disulfide containing 30 g of acetyl chloride. Aluminum chloride (43 g, 0.33 mol) was added slowly and the mixture was stirred at 25° for 12 hr on a steam bath for 2 hr. After cooling 100 ml of water was added cautiously. The carbon disulfide was removed by distillation and the residual aqueous layer extracted with ether. The ethereal extracts were washed with 5% aqueous KOH and dried over Na_2SO_4. Distillation gave 30 g (50%) of 2-methyl-4,5-dimethoxyacetophenone, bp 204° at 70 Torr. The acetophenone (20 g, 0.11 mol) was added to 100 g of 5% zinc–mercury amalgam in 200 ml of concentrated hydrochloric acid. After heating for 15 hr the mixture was cooled and extracted with chloroform. The chloroform solution was washed with aqueous KOH and dried over Na_2SO_4. The solvent was removed and the residual oil was distilled to yield 14 g (78%) of 4-methyl-5-ethyl-1,2-dimethoxybenzene, bp 105° at 5 Torr. The dimethoxybenzene derivative (5 g) was dissolved in 75 ml of hydriodic acid (specific gravity = 1.5) and the mixture refluxed under nitrogen for 1 hr. After cooling and diluting with water, the

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aqueous solution was extracted with chloroform. The extracts were dried over $CaCl_2$ and the chloroform was removed to yield 4-methyl-5-ethylcatechol: ir (neat) 3450 cm^{-1} (OH); pmr (CCl_4) δ 1.0 (t, 3), 2.0 (s, 3), 2.25 (q, 2), 6.05 (m, 2), 6.50 (s, 2); mass spectrum (70 eV) *m/e* 152 (parent ion). The diacetate had a mp of 70–74°, lit.[79] mp 72–73°.

6-Methyltricyclo[5.2.0^{1,7}.0^{2,7}]decan-4-one was prepared by photolysis of $\Delta^{1,9}$-10-methyl-2-octalone.[80] A solution of 5.1 g of the ketone in 750 ml of methanol was irradiated for 80 hr with a Hanovia 550-W lamp. The product was isolated by silica gel chromatography (elution with 5% ether in hexane) and purified by glpc (SF-96 on Chromosorb W at 160°).

Dihydrolumisantonin was prepared by the photolysis of santonin to lumisantonin (mp 156–159°, lit.[81] mp 156–157°) followed by hydrogenation in ethyl acetate using a palladium on charcoal catalyst to give the dihydro product: mp 162–166° (lit.[81] mp 164–165°); ir ($CHCl_3$) 1780, 1710 cm^{-1} (C=O).

Dimethyl bicyclo[2.1.0]pentane-*endo,endo*-2,5-dicarboxylate (precursor to **33b**) was prepared by the LAH reduction of 7-chloronorbornadiene (Frinton Laboratories) to a mixture of tricyclo[2.2.1.0^{2,7}]hept-2-ene and norbornadiene.[82] The crude mixture (2 g) was ozonized in 50 ml of methanol at −75° until a purple color persisted in solution. The methanol was removed at reduced pressure and the residue dissolved in 25 ml of 90% formic acid. When 15 ml of 30% hydrogen peroxide was added, an exothermic reaction took place. The solution was stirred for 40 min and then refluxed for 30 min. After cooling, the solvent was removed under vacuum. The residue was dissolved in 200 ml of ether and dried ($MgSO_4$), and the solution concentrated to 50 ml. To this solution was added a solution of diazomethane prepared from 16 g of Diazald in 200 ml of ether. After 16 hr at 25°, the excess diazomethane was destroyed by acetic acid. The ethereal solution was washed with saturated aqueous $NaHCO_3$ and saturated NaCl. After drying ($MgSO_4$) the ether was removed at reduced pressure leaving 1.7 g of an oil that was purified by glpc (15% Carbowax 20M on Chromosorb W at 180°): ir (neat) 3060 (cyclopropyl CH), 1728 cm^{-1} (C=O); pmr (CCl_4) δ 1.66 (t, 1, J = 6 Hz), 1.9–2.6 (m, 4), 3.1–3.4 (m, 1), 3.52 (s, 3), 3.61 (s, 3); mass spectrum (70 eV) *m/e* 184, 153, 125.

Tricyclo[3.3.0.0^{2,8}]octan-3-one (precursor to 33c) was prepared from the cyclopentene-3-acetic acid by the ring closure procedure of Fawzi and Gutche in 67% yield.[15] The ketone had bp 62–63° at 1.3 Torr: ir(neat) 3050 (cyclopropyl CH), 1723 cm^{-1} (C=O); pmr (CCl_4) δ 1.3–3.1; mass spectrum (70 eV) *m/e* 122 (parent ion). The 2,4-dinitrophenylhydrazone had mp 163.5–165.0°, lit.[17] mp 163–165°.

Anal. Calcd for $C_{14}H_{14}N_4O_4$: C, 55.62; H, 4.63. Found: C, 55.45; H, 4.59.

Tricyclo[3.3.1.0^{2,9}]nonan-3-one[16] (precursor to **33d**) was prepared from cyclohexene-3-acetic acid. 3-Bromocyclohexene was converted to cyclohexene-3-acetic acid *via* the malonic ester chain extension[83] followed by hydrolysis and decarboxylation. The acid had bp 97–99° at 0.4 Torr; amide mp 147–148° (lit.[16] mp 149–150°). The tricyclic ketone, bp 74° at 1.5 Torr, which was obtained in 37% yield from the acid gave an oxime with mp 89–90° (lit.[16] mp 90–91°): ir (neat) 3050 (cyclopropyl CH), 1710 cm^{-1} (C=O); pmr (CCl_4) δ 1.0–3.0; mass spectrum (70 eV) *m/e* 136 (parent ion).

Tricyclo[5.2.1.0^{2,10}]decan-9-one (precursor to **33e**) was prepared from 3-bromocycloheptene *via* the malonic ester synthesis to give cycloheptene-3-acetic acid. The amide of the acid had mp 130°; lit.[84] mp 128–129°. Ring closure yielded the ketone: bp 80° at 0.9 Torr; oxime mp 105–108° (lit.[84] mp 106–108°); ir (neat) 3060 (cyclopropyl CH), 1710 cm^{-1} (C=O); pmr (CCl_4) δ 1.0–3.0; mass spectrum (70 eV) *m/e* 150 (parent ion).

Tricyclo[4.3.1.0]decan-7-one was prepared by the Simmons–Smith methylene addition reaction of 4,5,6,7-tetrahydro-1-indanol. 4,5,6,7-Tetrahydro-1-indanone was prepared;[85] 2,4-dinitrophenylhydrazone, mp 231–232°, lit.[86] mp 229–230°. The corresponding allylic alcohol (obtained by LAH reduction) was converted to the tricyclic alcohol in 49% yield. The tricyclic ketone was obtained in 92% yield upon oxidation of the alcohol with chromium trioxide in pyridine, bp 78–80° at 2 Torr. The ketone was purified by glpc (20% DEGS on Chromosorb W at 153°): ir (CCl_4) 3065 and 1022 (cyclopropyl), 1715 cm^{-1} (C=O) (lit.[87] 3065, 1715 cm^{-1}); pmr (CCl_4) δ 0.85–2.50; 2,4-dinitrophenylhydrazone, mp 174–175°; semicarbazone, mp 189–190° dec.

Anal. Calcd for $C_{10}H_{14}O$: C, 80.00; H, 9.33. Found: C, 79.96; H, 9.41.

Tricyclo[4.3.1.0]dec-3-en-8-one was prepared from 4,7-dihydroindan-2-ol[88] by the Simmons–Smith reaction. 2-Indanol was prepared by the reduction of indene oxide (Columbia Chemical Co.) using a Raney nickel catalyst. 2-Indanol, mp 67–70° (lit.[89] mp 68.0–69.5°), was reduced with sodium in ethanol–liquid ammonia in 70% yield to 4,7-dihydroindan-2-ol, bp 100° at 1.5 Torr. Methylene addition proceeded in 85% yield to give the tricyclic alcohol, mp 68–70° (lit.[88] mp 69–70°). Oxidation with chromium trioxide in pyridine gave the tricyclic ketone,[90] bp 73° at 1.5 Torr: ir (neat) 3050 (cyclopropyl CH), 1740 cm^{-1} (C=O); pmr (CCl_4) δ 0.17 (m, 1), 0.90 (m, 1), 2.31 (m, 8), 5.55 (m, 2); mass spectrum (70 eV) *m/e* 148 (parent ion).

9-Methyltricyclo[4.3.1.0]decan-7-one was prepared from 9-methylbicyclo[4.3.0]non-1-en-7-one.[86] The ketone synthesized from cyclohexene and crotonic acid[86] (2,4-dinitrophenylhydrazone, mp 242.5–243°; lit.[86] mp 244°) was reduced with LAH to the allylic alcohol (bp 94–95° at 3.9 Torr) which yielded 68% tricyclic alcohol *via* the Simmons–Smith reaction; bp 105–106° at 4.9 Torr. Oxidation of the alcohol with chromium trioxide in pyridine gave the ketone: bp 101–102° at 5 Torr; ir (CCl_4) 3065, 1025 (cyclopropyl), 1720 cm^{-1} (C=O); pmr (CCl_4) δ 0.9–2.5 (m, 13), 1.07 (d, 3, J = 6 Hz); 2,4-dinitrophenylhydrazone, mp 177.0–177.5°.

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.20; H, 9.72.

Dimethyl *cis*-carboxycyclopropaneacetic acid[91] was prepared by ozonolysis of bicyclo[3.1.0]hex-2-ene. Bicyclo[3.1.0]hexan-2-ol was prepared[92] and converted to the xanthate[93] which was pyrolyzed to the olefin,[94] bp 70–73°; lit.[94] bp 70–71°. The olefin (1.7 g) in 35 ml of ethyl acetate was cooled to −76° and ozonized until the purple color persisted. The solvent was removed under vacuum and the residue added to 24 ml of 90% formic acid. After the addition of 8 ml of 30% hydrogen peroxide, the solution was stirred at 60° for 6 hr and at 25° for 12 hr. The solvent was removed under vacuum and benzene added and removed by vacuum. The residue was dissolved in 20 ml of ether and diazomethane from 13 g of Diazald in 150 ml of ether distilled into the solution. The ester was isolated by glpc (15% Carbowax 20 M, Chromosorb W at 150°): pmr (CCl_4) δ 0.8–1.9 (m, 4), 2.55 (d, 2, J = 6.5 Hz), 3.62 (s, 6).

2,3-Bis(trimethylsiloxy)bicyclo[3.1.0]hex-2-ene was prepared by the acyloin condensation of the dimethyl ester of *cis*-carboxycyclopropaneacetic acid in the presence of trimethylchlorosilane.[95] To a suspension of 0.25 ml of 1:3 sodium–potassium alloy in 25 ml of ether, there was added 1.5 ml of trimethylchlorosilane and 80 μl of the diester. The suspension was stirred under nitrogen for 1.5 hr at 0°. The suspension was filtered and the solvent removed under vacuum. The crude olefin appeared to decompose slowly at room temperature and further purification was not attempted. Upon dissolving 40 μl of the crude bis(trimethylsiloxy)alkene in 0.8 ml of DMSO containing 20 mg of potassium *tert*-butoxide a strong esr signal of **6** was obtained.

Bicyclo[4.1.0]heptan-2-one was prepared according to the procedure of Dauben and Berezin.[92] The material was purified by preparative glpc (15% Carbowax 20 M on Chromosorb W, 168°): ir 3050, 1026 (cyclopropyl), 1695 cm^{-1} (C=O); pmr (CCl_4) δ 0.78–1.26 (m, 2), 143–2.22 (m, 8). The ketone gave a 2,4-dinitrophenylhydrazone, mp 164–166°, lit.[92] mp 159–161.5°.

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5,5-Dimethylbicyclo[4.1.0]heptane-2,3-dione was prepared from the Simmons–Smith reaction on the allylic alcohol. 4,4-Dimethyl-2-cyclohexanone was prepared;[96] 2,4-dinitrophenylhydrazone mp 139–141°, lit.[97] mp 142°. The ketone was reduced with LAH to the allylic alcohol, bp 92.0–92.5° at 25 Torr. The Simmons–Smith reaction proceeded to give 77% bicyclic alcohol, bp 100–101° at 20 Torr. Oxidation of the bicyclic alcohol with chromium trioxide in pyridine gave 77% of the ketone, bp 98–100° at 15 Torr; 2,4-dinitrophenylhydrazone mp 141–142°; ir (CCl_4) 3070, 1025 (cyclopropyl), 1685 cm^{-1} (C=O); pmr (CCl_4) δ 0.80–2.20 (m, 8); 1.12 (s, 6). The ketone (1.5 g) in 20 ml of 95% ethanol was oxidized with 1.3 g of selenium dioxide. The mixture was refluxed for 20 hr, diluted with 75 ml of methanol, and filtered through Celite. The solvent was evaporated under vacuum and the residue dissolved in ether and dried ($MgSO_4$). The ether was evaporated and the residue chromatographed on silica gel. Hexane (95%)–ether (5%) eluted 154 mg of a crystalline material, mp 75–77° from pentane: ir (KBr) 3400, 1660, 1640, 1365, 1020 cm^{-1}; pmr ($CDCl_3$) 0.65–0.95 (m, 1), 1.30–2.25 (m, 3), 1.21 (s, 3), 1.29 (s, 3), 5.43 (d, 1, J = 2 Hz), 5.90 (s, 1); mass spectrum (70 eV) *m/e* 152 (parent ion).

Anal. Calcd for $C_9H_{12}O_2$: C, 71.00; H, 7.90. Found: C, 69.60; H, 7.93.

4,4,6-Trimethylbicyclo[4.1.0]heptan-2-one was prepared by the reduction of isophorone with lithium aluminum hydride to the corresponding allylic alcohol, bp 63–64° at 20 Torr, followed by the Simmons–Smith reaction on the allylic alcohol to give 4,4,6-trimethylbicyclo[4.1.0]heptan-2-ol, bp 90–91° at 11 Torr (the two alcohols were not analytically pure but nmr and ir data were consistent with the structures), and oxidation of this bicyclic alcohol with chromium trioxide in pyridine to give the desired ketone, bp 85–87° at 9 Torr: ir (CCl_4) 3040, 1015 (cyclopropyl), 1690 cm^{-1} (C=O); pmr (CCl_4) δ 0.94 (s, 6), 1.18 (s, 3), 0.80–1.90 (m, 7); mass spectrum (70 eV) *m/e* 152 (parent ion); 2,4-dinitrophenylhydrazone, mp 128.0–129.5°.

Bicyclo[5.1.0]octan-2-one was prepared by the Simmons–Smith reaction with 3-cycloheptenol, bp 61–63° at 10 Torr, in 60% yield. Bicyclo[5.1.0]octan-2-ol, bp 90° at 10 Torr, mp 39–42° (lit.[92] mp 39–40°) was oxidized with Jones reagent in acetone to the ketone, bp 70° at 3.5 Torr; 2,4-dinitrophenylhydrazone, mp 192–195° (lit.[98] mp 195–196°): ir (neat) 3050 (cyclopropyl CH), 1695 cm^{-1} (C=O); pmr (CCl_4) δ 0.8–2.5; mass spectrum (70 eV) *m/e* 124 (parent ion).

Bicyclo[6.1.0]nonan-2-one was prepared in a similar fashion to bicyclo[5.1.0]octan-2-one to give a ketone, bp 55–57° at 0.8 Torr: ir (neat) 3010 (cyclopropyl CH), 1695 cm^{-1} (C=O), lit.[99] 1695 cm^{-1} (C=O); pmr (CCl_4) δ 0.4–2.5; mass spectrum (70 eV) *m/e* 138 (parent ion).

Tricyclo[4.4.1.0^{1,10}]undecan-2-one was prepared from $\Delta^{1,9}$-2-octalone[100] *via* reduction with $LiAlH_4$ to the allylic alcohol followed by the Simmons–Smith reaction on this allylic alcohol to give tricyclo[4.4.1.0^{1,10}]undecan-2-ol and oxidation of the tricyclic alcohol with Jones reagent in acetone. (Analytical samples of the alcohols were not obtained but the nmr and ir data were consistent with the structures proposed.) The pure ketone was obtained by glpc (15% Carbowax 20 M on Chromosorb W at 180°): ir (CCl_4) 3070, 1028 (cyclopropyl), 1685 cm^{-1} (C=O); pmr (CCl_4) δ 0.6–2.2; mass spectrum (70 eV) *m/e* 164 (parent ion); semicarbazone mp 213–215° dec.

Anal. Calcd for $C_{11}H_{16}O$: C, 80.52; H, 9.75. Found: C, 80.32; H, 9.75.

1-Methyltricyclo[4.4.1.0^{1,10}]undecan-2-one was prepared from $\Delta^{1,9}$-1-methyl-2-octalone (Aldrich Chemical Co.) *via* reduction to the allylic alcohol (bp 76–78° at 0.5 Torr), Simmons–Smith reaction to give 1-methyltricyclo[4.4.1.0^{1,10}]undecan-2-ol, and oxidation by Jones reagent. Pure material was isolated by glpc (15% Carbowax 20 M on Chromosorb W at 180°): ir (CCl_4) 3050, 1020 (cyclopropyl), 1680 cm^{-1} (C=O); pmr (CCl_4) δ 0.50 (t, 1, J = 5 Hz), 1.0–2.3 (m, 14), 1.2 (d, 3, J = 5 Hz); mass spectrum (70 eV) *m/e* 178 (parent ion). The semicarbazone had mp 203–204°.

Anal. Calcd for $C_{13}H_{21}N_2O$: C, 66.38; H, 8.93. Found: C, 66.17; H, 9.08.

Dimethyl *cis*-1,2-cyclopropanedicarboxylate was prepared from the anhydride,[101] mp 56–58° (lit.[101] mp 58–60°), which was hydrolyzed to the free acid, mp 140–142°, from nitromethane; lit.[101] mp 139–142°. Esterification with diazomethane in ether gave the desired ester which was purified by glpc (20% DEGS on firebrick at 165°): ir (CCl_4) 3070, 1045 (cyclopropyl), 1730 cm^{-1} (C=O); pmr (CCl_4) δ 0.96–2.12 (m, 4), 3.61 (s, 6).

1,5-Dimethyl-2,8-dicarbomethoxytetracyclo[3.3.0^{2,8}.0^{4,6}]octane (2)[102] was prepared by the literature procedure[9] by the benzophenone-sensitized photoaddition of 2-butyne to the anhydride of 1,4-cyclohexadiene-1,2-dicarboxylic acid.[103] The photoadduct, mp 159–160° (lit.[5] 157–158°), was converted to the monoester by methanol and to the diester with diazomethane. Material isolated by glpc (20% Carbowax 20 M on Chromosorb W at 170°) had ir and pmr spectra identical with that reported.[5]

Methyl *cis*-3-carbomethoxy-1,1-dimethylcyclopropane-2-propinate was obtained by oxidation[104] of an equilibrated mixture of 2- and 3-carene.[41] The mixture of diacids was esterified with diazomethane in ether and the desired ester isolated by preparative glpc on a column of 15% Carbowax 20 M at 150°. The desired ester had a retention time of 6 min whereas dimethyl 1,1-dimethylcyclopropane-*cis*-2,3-diacetate had a retention time of 12 min. The desired ester had ir (CCl_4) 1735, 1720 (C=O), 1525, 1255, 1162 cm^{-1}; pmr (CCl_4) δ 1.15 (s, 3), 1.10–1.50 (m, 3), 1.90 (d, 1, J = 18 Hz), 2.60–2.70 (m, 2), 3.57 (s, 3), 3.60 (s, 3); mass spectrum (70 eV) *m/e* 183, 155, 127. The diester was subjected to the acyloin condensation in the presence of trimethylchlorosilane. The crude bistrimethylsiloxyalkene was isolated by glpc (15% Carbowax 20 M, 150°) and converted to semidione **70** by treatment with potassium *tert*-butoxide in DMSO or DMSO-d_6.

Tricyclo[2.2.2.0^{2,6}]octane-7,8-dione (71) was prepared from a mixture of the 7- and 8-ones.[42] To a mixture of 1 g of the monoketone in 15 ml of 95% ethanol was added 1 g of SeO_2 and the mixture refluxed for 5 hr. The solvent was removed at reduced pressure and the residue, when dissolved in 100 ml of ether, treated with 2 g of freshly precipitated silver under reflux for 3 hr. The mixture was filtered, the ether evaporated under vacuum, and the residue sublimed at 80° (0.05 Torr) to give 470 mg (42%) of yellow solid, mp 153–155° from benzene–hexane: ir (KBr) 1740, 1705, 1690 (C=O), 1370, 1312, 1260, 1004, 960, 930, 852, 792, 750 cm^{-1}; pmr ($CHCl_3$) δ 2.0–2.5 (m, 7), 2.85–3.05 (m, 1); mass spectrum (70 eV) *m/e* 136, 108, 80, 79, 77.

Tricyclo[2.2.2.0^{2,6}]oct-7-ene was prepared[43] and a pure sample isolated by preparative glpc (15% Carbowax 20 M, 70°). The olefin (90 mg in 10 ml of methanol) was treated with ozone at −75° until the purple color persisted. The methanol was evaporated at reduced pressure and the residue added to 3 ml of 90% formic acid and 1 ml of 30% hydrogen peroxide. After stirring for 30 min the solution was refluxed for 30 min. The solution was cooled and the solvent removed under vacuum to leave white crystals which were treated with the diazomethane prepared from 2.5 g of Diazold in 65 ml of ether. The excess diazomethane was destroyed with acetic acid. The etheral solution was washed with water, saturated $NaHCO_3$, and saturated NaCl solutions before drying over $MgSO_4$. After distillation of the ester, pure **dimethyl *endo*-3,*syn*-6-bicyclo[3.1.0]hexanedicarboxylate (73)** was obtained by glpc (15% Carbowax 20 M, 180°): ir (neat) 3050 (cyclopropyl CH), 1725 (C=O) cm^{-1}; pmr (CCl_4) δ 1.60–2.35 (m, 7), 2.90–3.40 (m, 1), 3.60 (s, 6); mass spectrum (70 eV) *m/e* 198, 167, 166, 139, 138, 107, 79.

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