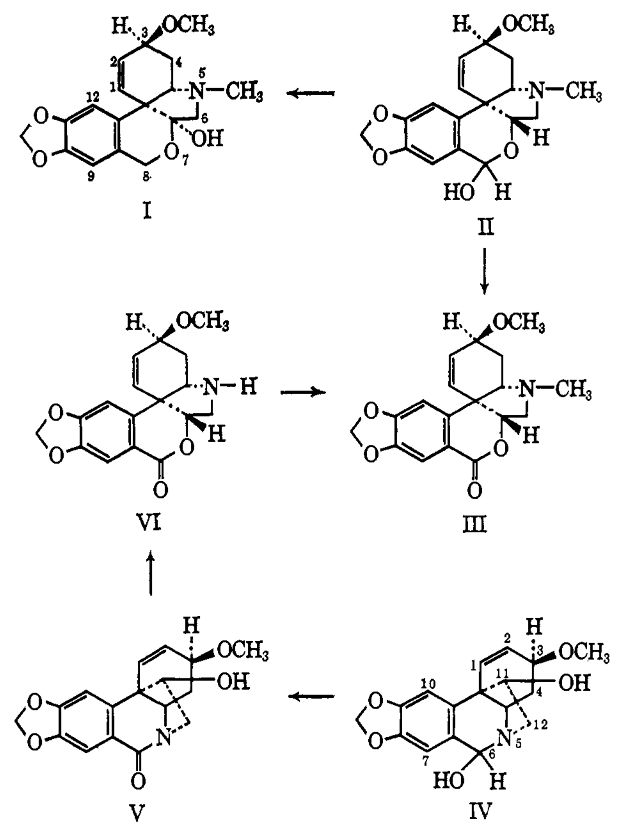

ment to tazettine but also by its oxidation to III with manganese dioxide. Compound III was synthesized from haemanthidine (IV) by manganese dioxide oxidation[11] to oxohaemanthidine (V) and rearrangement to VI, mp 133–134°, $[\alpha]^{24}\text{D}$ +207° (c 0.36, $CHCl_3$), in aqueous acetic acid and sodium acetate. N-Methylation of VI with formaldehyde and sodium borohydride provided III, mp 127–128°, $[\alpha]^{24}\text{D}$ +276° (c 0.95, $CHCl_3$), identical in all respects with the manganese dioxide oxidation product of pretazettine.[12]

[11] S. Uyeo, H. M. Fales, R. J. Highet, and W. C. Wildman, *J. Am. Chem. Soc.*, **80**, 2590 (1958).

[12] Preliminary research on the conversion of IV to III was carried out by Professor S. Uyeo at the National Heart Institute in 1958. The facile lactam–lactone rearrangement appears to relieve the considerable internal strain of V.

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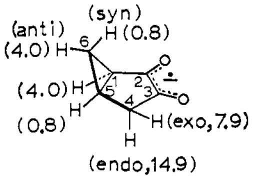
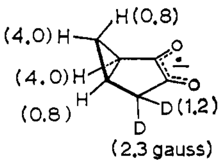
Application of Electron Spin Resonance Spectroscopy to Problems of Structure and Conformation. XI. Bicyclo[3.1.0]hexane Semidiones[1]

Sir:

Oxidation of a 2- or 3-oxobicyclo[3.1.0]hexane in basic dimethyl sulfoxide (DMSO) solution yields a semidione showing hyperfine splitting by six hydrogen atoms (**1**).[2] In DMSO-d_6, the 3-ketone gave semidione **2** while the 2-ketone yielded semidione **3**. Semidione **2** must result from hydrogen–deuterium exchange prior to oxidation. The stereoselective hydrogen–deuterium exchange observed in **3** occurs after oxidation and may be a property of the very weakly acidic radical anion. Stereoselective hydrogen–deuterium exchange was not found in either of the monoketones under the reaction conditions. The second methylene hydrogen in **3** will exchange in 8 hr at 25° under our reaction conditions. The 6,6-dimethyl derivative exchanges only the *endo*-hydrogen atom, even after 18 hr at 25°. The 1,5-dialkyl and the *anti*-6-alkyl derivatives also exchange the *exo*-methylene hydrogen atom at a lower rate than the unsubstituted compound. No exchange at the bridgehead positions was detected.



1



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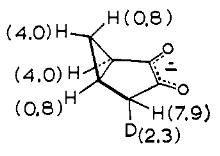

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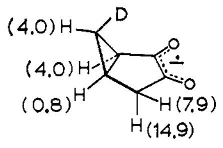
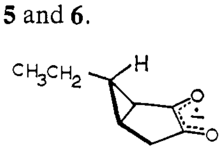


4

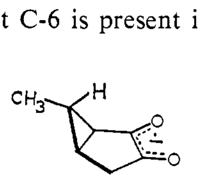
The 1-isopropyl-4-methylbicyclo[3.1.0]hexane-2,3-semidiones derived from β-dihydroumbellulone (*exo*-methyl) and thujone (*endo*-methyl) isomerize slowly in DMSO containing potassium *t*-butoxide to give a mixture containing approximately 90% *endo*-methyl (a^H = 6.2, 4.8, 0.8, and 0.6 gauss) and 10% *exo*-methyl (a^H = 13.9, 4.9, 0.7, and 0.6 gauss) isomers.

The assignment of hfsc to the hydrogen atoms at the C-6 position is based on semidiones **4–6** derived from the corresponding 2- or 3-ketones.[3] The 4-gauss hydrogen splitting at C-6 is present in **4** and absent in **5** and **6**.



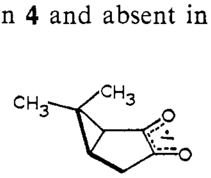
5

a^H = 14.7, 7.8, 4.2, 0.35 gauss
$a_{CH_2}{}^H$ = 0.75 gauss



6

a^H = 14.6, 7.6, 4.3, 0.9 gauss
$a_{CH_3}{}^H$ = 0.4 gauss



7

a^H = 14.6, 7.6, 5.1, 0.9 gauss
$a_{CH_3}{}^H$ = 0.45 (one) gauss

Not only do *anti* hydrogens at C-6 interact with the unpaired spin (a double V arrangement)[4–6] but hydrogen atoms attached to alkyl groups in the *anti* C-6 position (**5**, **6**, **7**) also interact *via* 2.5 V arrangements (**8**). Even larger 2.5 V (four-bond) interactions are expected and seen in the rigid semidiones derived from

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[1] This work was supported by grants from the National Science Foundation (GP-6402X) and the Army Research Office (Durham) (DA-ARO-D-31-124-G867).

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

[3] The ketonic precursor to **4** was prepared from *syn*-6-deuteriobicyclo[3.1.0]hexane-3-carboxylic acid: P. G. Gassman and F. V. Zalar, *Tetrahedron Letters*, **43**, **44**, 3251 (1964). The 2-ketone precursors to **5** and **6** were prepared by the ring closure of *trans*-RCH=CHCH$_2$CH$_2$COCHN$_2$: M. M. Fawzi and C. David Gutche, *J. Org. Chem.*, **31**, 1390 (1966).

[4] G. A. Russell and K.-Y. Chang, *J. Am. Chem. Soc.*, **87**, 4381 (1965).

[5] G. A. Russell, K.-Y. Chang, and C. W. Jefford, *ibid.*, **87**, 4383 (1965).

[6] G. A. Russell, G. Holland, K.-Y. Chang, and L. H. Zalkow, *Tetrahedron Letters*, 1955 (1967).

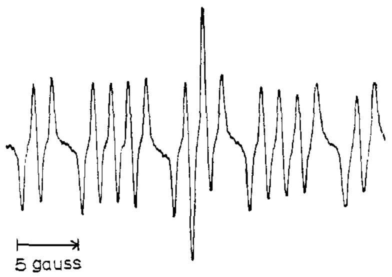
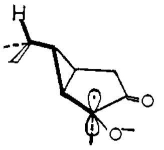
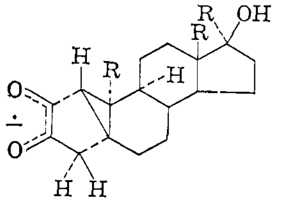


Figure 1. First-derivative esr spectrum obtained by exposure of phototestosterone to a trace of oxygen in dimethyl sulfoxide solution containing potassium *t*-butoxide.

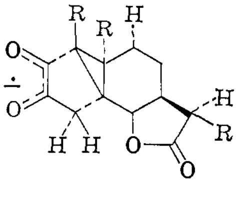
phototestosterone (**9**) and dihydrolumisantoin (**10**) (Figure 1). The *trans* coplanar arrangement required for a maximum in this long-range hyperfine splitting is illustrated by the fact that only one of the γ-methylene hydrogen atoms interact in **10**.



8



9, R = CH_3
a^H = 13.9, 7.6, 4.8, 1.5 gauss



10, R = CH_3
a^H = 14.3, 7.6, 1.1 gauss

Semidiones **7**, **9**, and **10**, as well as numerous other derivatives, have been observed to undergo the stereospecific hydrogen–deuterium exchange at C-4.

The application of esr spectroscopy as a tool in the proof of structure of bicyclic ketones is obvious.

Acknowledgment. β-Dihydroumbellulone was graciously supplied by Professor R. H. Eastman. The esr spectrum of **9** was obtained by Dr. E. R. Talaty and spectra of additional derivatives of **9** and **10** have been obtained by Dr. R. S. Givens.

[7] National Aeronautics and Space Administration Predoctoral Fellow, 1965–1967.

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Application of Electron Spin Resonance Spectroscopy to Problems of Structure and Conformation.
XII. Molecular Rearrangements in the Bicyclo[3.1.0]hexane Semidiones[1]

Sir:

Oxidation of *syn*- or *anti*-6-ethylbicyclo[3.1.0]hexan-2-one[2,3] in basic dimethyl sulfoxide (DMSO) solution yields the same semidione whose hyperfine splitting constants[4] are consistent with the more stable *anti* structure (Figure 1).

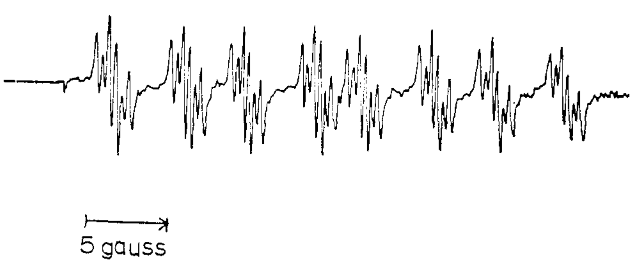
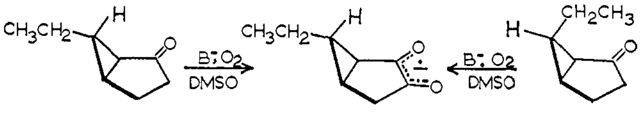
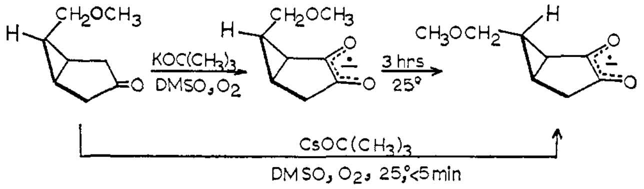


Figure 1. First-derivative esr spectrum of radical anion produced by exposure of *syn*- or *anti*-4-ethylbicyclo[3.1.0]hexan-2-one to a trace of oxygen in dimethyl sulfoxide solutions containing potassium *t*-butoxide.

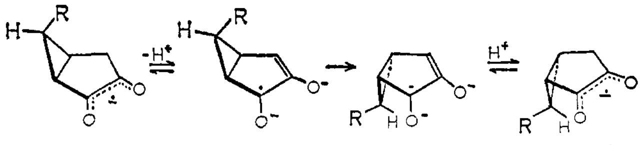
Oxidation of *syn*-6-(methoxymethyl)bicyclo[3.1.0]hexan-3-one[3,5] in DMSO containing potassium *t*-butoxide initially yields a complex esr signal that slowly (3 hr) converts to a pure signal whose hfsc are consistent with the *anti* structure (a^H = 14.65, 7.75, 4.22, 0.75 (2 H), and 0.35 gauss). It is tempting to assume that the mixture of radical anions first observed consists of the *anti* semidione and its unrearranged C-6 epimer. Oxidation in the presence of the stronger base cesium *t*-butoxide, forms the *anti* semidione with no indication of the formation of an initial mixture of radicals (spectrum recorded 5–10 min after oxygenation).



a^H = 14.7, 7.8, 4.2, 0.35 gauss
$a_{CH_2}{}^H$ = 0.75 gauss



The 6-ethylbicyclo[3.1.0]hexan-2-ones do not epimerize under the reaction conditions if oxygen is excluded. An epimerization mechanism involving ionization of the cyclopropyl hydrogen atoms apparently can be eliminated since the semidione of bicyclo[3.1.0]hexan-3-one in DMSO-d_6 does not show any hydrogen–deuterium exchange at the cyclopropyl positions.[6] Epimerization at C-6 may involve a ring flip at either the diketone, radical-anion, or the radical-dianion state. The effect of base seems most consistent with the radical dianion. Of course the ring flip depicted must involve the uncoupling and re-formation of the C-1–C-5 bond.[7] Alternately the rupture and closure of the C-1–C-6 or C-5–C-6 bonds can be involved.



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[1] This work was supported by grants from the National Science Foundation (GP-6402X) and the Army Research Office (Durham) (DA-ARO-D-31-124-G867).

[2] Prepared by ring closure reactions of *cis*- and *trans*-$CH_3CH_2CH{=}CHCH_2CH_2COCHN_2$.

[3] Satisfactory analyses and spectral data were obtained for all new compounds.

[4] G. A. Russell, P. R. Whittle, J. McDonnell, *J. Am. Chem. Soc.*, **89**, 5515 (1967).

[5] Prepared from the *syn*-6-carboxaldehyde of bicyclo[3.1.0]hexene: J. Meinwald, S. S. Labana, and M. S. Chadha, *J. Am. Chem. Soc.*, **85**, 582 (1963).

[6] Epimerization at C-6 appears to require a steric driving force since no significant amount of epimerization for the *syn*-6-deuterio semidione is detected within 10 hr.