

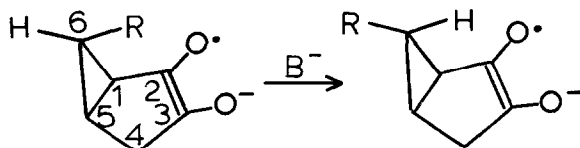
RING INVERSION IN THE ISOMERIZATION OF SYN- TO ANTI-
6-ALKYLBICYCLO[3.1.0]HEXANESEMEDIONES

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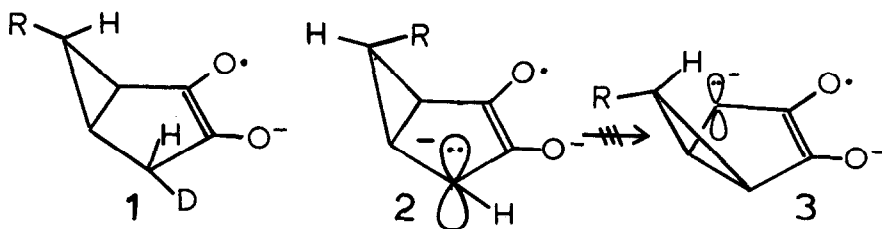
We have previously postulated (1,2) the rearrangement of syn-6-ethylbicyclo[3.1.0]hexanesemidione to the anti isomer.



We have now found that the syn-6-methyl semidione is much more stable and that isomerization to the anti isomer can be followed by esr spectroscopy. The rearrangement with R = methyl proceeds to completion in dimethyl sulfoxide in the presence of potassium t-butoxide in 3 hrs, whereas the rearrangement of the syn-ethyl compound occurs in 1 min under similar conditions. The steric driving force is emphasized by the observation that the syn-6-deuterium compound does not show the rearrangement.

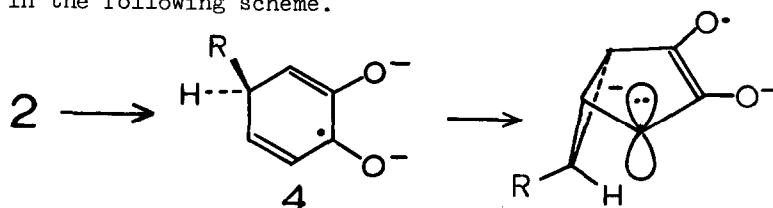
Figures 1A and 1B give the distinctly different esr spectra of the syn- and anti-6-methylbicyclo[3.1.0]hexanesemidiones.

A radical dianion is implicated as an intermediate since the epimerization occurs much more rapidly in the presence of the stronger base cesium t-butoxide than in the presence of potassium t-butoxide. Ionization of the hydrogen atom at C-6 is excluded since in d_s-DMSO only the quasi-axial α -methylene hydrogen is exchanged to yield 1. Intermediate 2 is thus suggested.

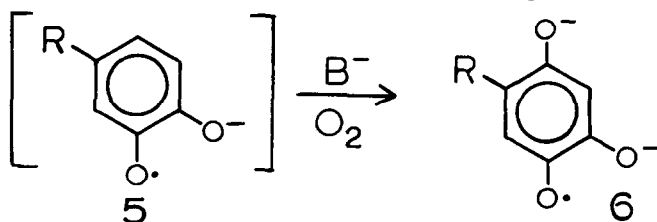


A sigmatropic 1,4-rearrangement, between carbon atom 1 and 4 to form 2 can be eliminated since 1-deuterio-syn-6-ethylbicyclo-2-one upon oxidation quite clearly produced 1-deuterio-anti-6-ethylbicyclohexane-2,3-semidione.

We thus believe that the isomerization involves a ring inversion as shown in the following scheme.

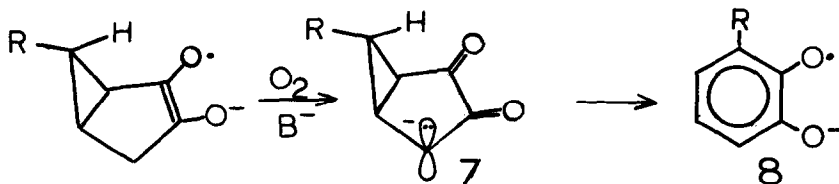


The reclosure of 4 to yield the isomerized semidione is apparently not a highly efficient process. Thus, when a solution in which the rearrangement has proceeded to completion is exposed to an excess of oxygen, the semidione is destroyed and an o-semiquinone is formed. From syn-6-ethyl- and syn-6-methyl-bicyclo[3.1.0]hexane-2-one we observe semiquinone 6, presumably a further oxidation product of 5 (3).



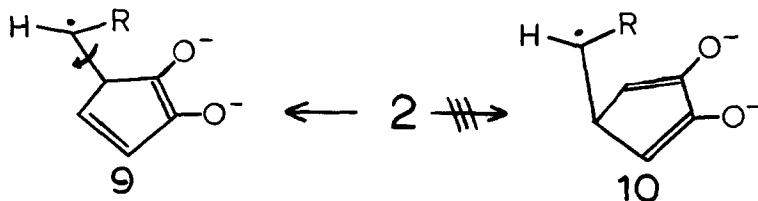
This behavior is in marked contrast to that of the anti-6-alkyl ketone and semidione. Over-oxidation of the semidione prepared from the anti-6-methyl or anti-6-ethyl-2-ketone yields solely the 3-alkyl

o-semiquinone (2). The carbon atom originally at C-6 has migrated to the C-3 position of the semiquinone to yield 8. Similar results were obtained with substituents at C-1 and C-5 and the reaction has been explained as a sigmatropic 1,4-rearrangement (from C-5 to C-2) of the enolate anion of the diketone (2). This rearrangement yields a cyclopropanol anion which



can undergo ring opening to yield 8 (Figure 1c). Both 6 and 8 have been observed starting with the syn-6-alkyl ketone but only 8 from the anti-6-alkyl ketone. It is of interest to speculate that perhaps orbital symmetry arguments can explain the apparent observation that 7 but not 2 undergoes a sigmatropic 1,4-bond rotation (4).

The formation of a precursor to 6 from only the syn-6-alkyl ketone appears to eliminate 9 as a reaction intermediate for the rearrangement to the anti-6-alkyl semidione. The result with the 1-deuterio substituent eliminates 10 unambiguously.



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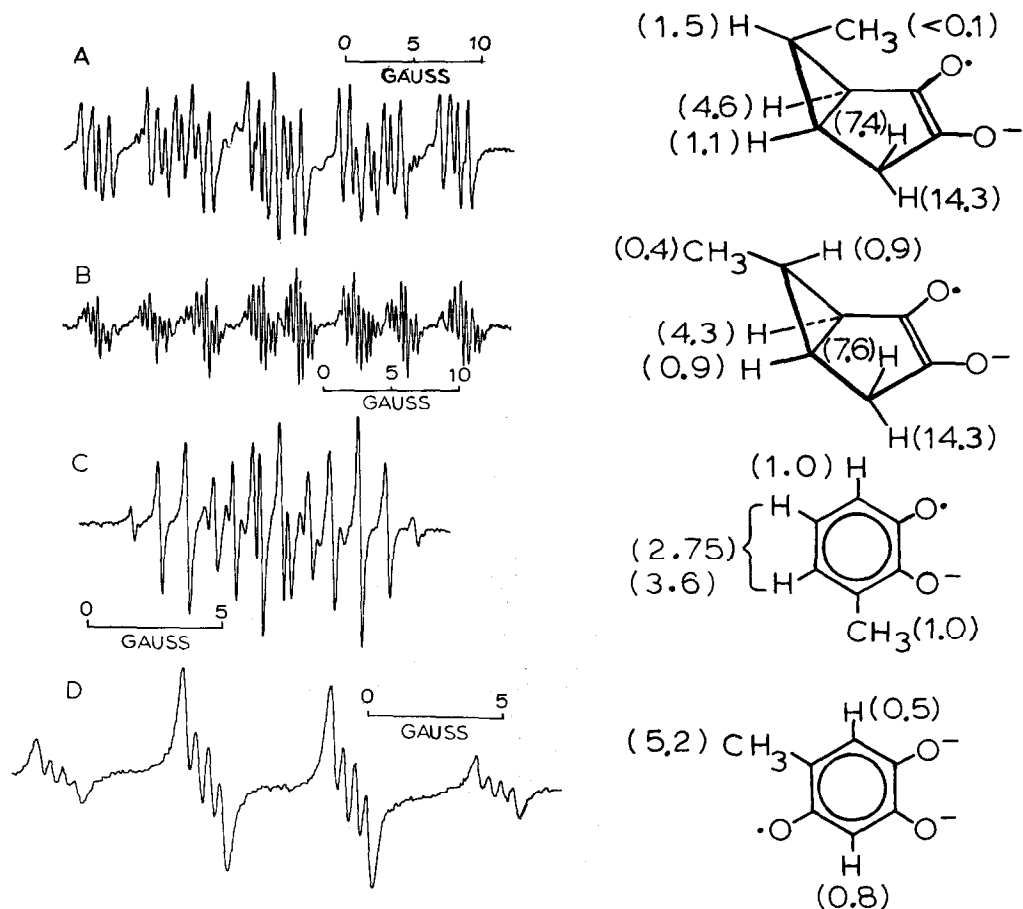


Figure 1.- Radical anions observed in the oxidation of syn- and anti-6-methyl-bicyclo[3.1.0]hexan-2-one in dimethyl sulfoxide solution: A, initial oxidation product of syn-6-methyl ketone in presence of a 200% excess of potassium t-butoxide; B, rearrangement product of A (3 hrs) or initial oxidation product of the anti-6-methyl-2-ketone; spectrum B also formed rapidly from the syn-6-methyl-2-ketone in presence of 200% excess of cesium t-butoxide; C, spectrum observed by further oxidation of anti-6-methyl-2-ketone; D, spectrum observed by oxidation of the syn-6-methyl-2-ketone past the semidione stage. Spectrum D observed with both cesium and potassium t-butoxide. Still further oxidation destroys D and generates spectrum C.