

PERICYCLIC REACTIONS OF SOME ENOLATE IONS

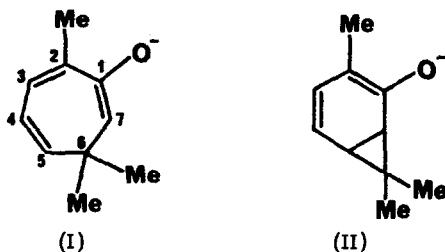
by A. J. Bellamy and W. Crilly

Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh,

EH 9 3JJ.

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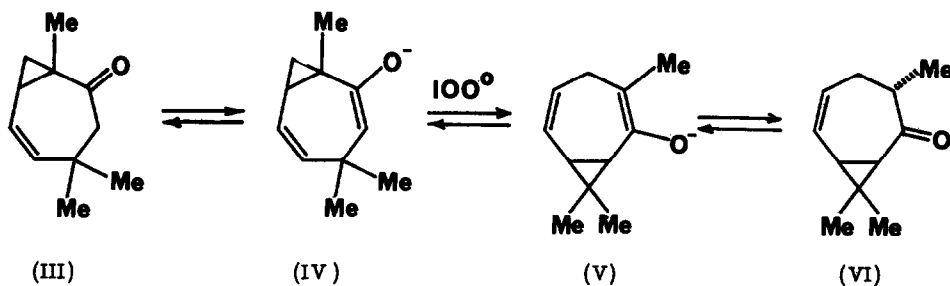
The formation of bicyclic products from the enolate ion of eucarvone (I) e.g. alkylation, is generally considered to proceed via the bicyclic enolate ion, II,<sup>1</sup> involving a hexatriene-cyclohexadiene disrotatory electrocycloisalisation. We wish to report here the direct observation of the interconversion of these anions by n.m.r. spectroscopy. A solution of the enolate ions was generated by treating eucarvone<sup>2</sup> with sodium hydride in dioxan, followed by removal of the insoluble material. The n.m.r. spectrum of the solution at 28° was interpreted as a time-averaged spectrum of the two anions:  $\delta$  6.001 (d, 3-H), 5.348 (t, 4-H), 3.332 (t, 5-H), 2.630 (d, 7-H) ( $J_{3,4}$  5.5Hz,  $J_{4,5}$  6.56Hz,  $J_{5,7}$  7.38Hz), 1.988 (s, 2-Me), and 1.125 (s, 6-Me<sub>2</sub>) (numbering as for I). From the chemical shift of 5-H in the averaged spectrum, and using the chemical shift of 5-H in eucarvone itself ( $\delta$  6.14), and of 6-H in 3-methylcar-4-en-2-one<sup>1a</sup> ( $\delta$  1.93) as approximate values for 5-H in I and 6-H in II respectively, we calculate that the equilibrium mixture of I and II contains  $\sim$  67% of II.



Methylation of the anion mixture with methyl iodide at 20° gave 3-methylcar-4-en-2-one and 2,6,6,7-tetramethylcyclohepta-2,4-dienone<sup>1a</sup> in the ratio  $\sim$  4:1, irrespective of whether the methyl iodide was present during, or was added after, the generation of the anion. The anion II is therefore about twice as reactive as anion I.

The ketone III, prepared from eucarvone by the method of Corey and Chaykovsky,<sup>3</sup> was also found to undergo a pericyclic reaction i.e. Cope rearrangement, when converted to its enolate ion, IV c.f. homotropilidine.<sup>4</sup> In this case, the

interconversion of the two enolate ions is slow even at  $150^{\circ}$ , presumably due to the necessity to adopt a crowded cisoid conformation before rearrangement can occur. The n. m. r. spectrum of the equilibrated anions, IV and V, in diphenyl ether at  $150^{\circ}$  showed separate absorptions for the two species, in the ratio of 4:5. Quenching the anion mixture (in dioxan) with acetic acid in ether enabled us to isolate the two isomeric ketones, III and VI.



### References

- 1 a) A. J. Bellamy and W. Crilly, J. C. S. Perkin II, 1972, 395;  
 b) A. J. Bellamy, J. Chem. Soc. (B), 1969, 449; c) E. J. Corey, H. J. Burke and W. A. Remers, J. Amer. Chem. Soc., 1956, 78, 180.
- 2 E. J. Corey and H. J. Burke, ibid., 174.
- 3 E. J. Corey and M. Chaykovsky, ibid., 1965, 87, 1353.
- 4 W. von E. Doering and W. R. Roth, Angew. Chem. Int. Ed., 1963, 2, 115; Tetrahedron, 1963, 19, 715; L. Birladeanu, D. L. Harris and S. Winstein, J. Amer. Chem. Soc., 1970, 92, 6387.