Tetrahedron Letters No. 10, pp 883 - 886, 1972. Pergamon Press. Printed in Great Britain.

VARIABLE TEMPERATURE CIRCULAR DICHROISM OF 6-METHYLSPIRO[4·4]NONAN-1-ONE.
AN APPROACH TO FRONT OCTANTS.

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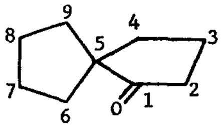
(Received in USA 20 January 1972; received in UK for publication 31 January 1972)

Spiro[4·4]nonan-1-one (1) is incapable of exhibiting optical activity; however, the introduction of a methyl group at C-6 generates a chiral center, the carbonyl chromophore becomes dissymmetrically perturbed and the Octant Rule is applicable.[1,2] A careful examination of Dreiding and Fischer-Hirschfelder models made of the two possible isomeric 6-methylketones, _cis_-6-methylspiro[4·4]nonan-1-one (2) and _trans_-6-methylspiro[4·4]nonan-1-one (3), yields the intriguing observation that the methyl group of 2 lies in a front octant[3] or at least in or near the third symmetry plane (orthogonal to and bisecting the C=O axis) of the Octant Rule.[1,2] In order to examine this possibility experimentally, we prepared both (-)-2 and (-)-3 from a



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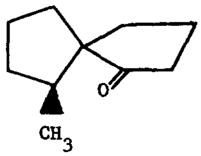

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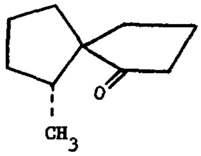

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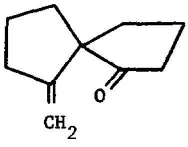

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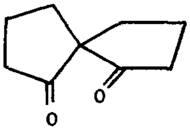

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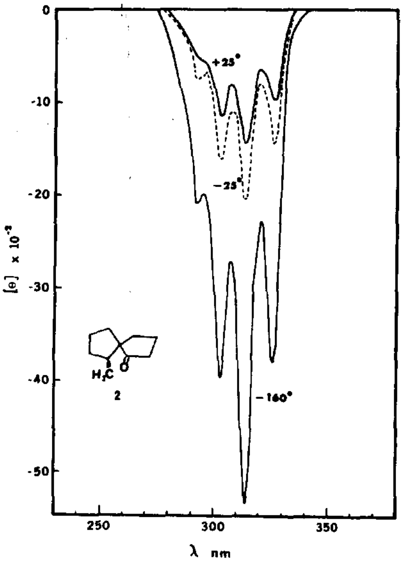
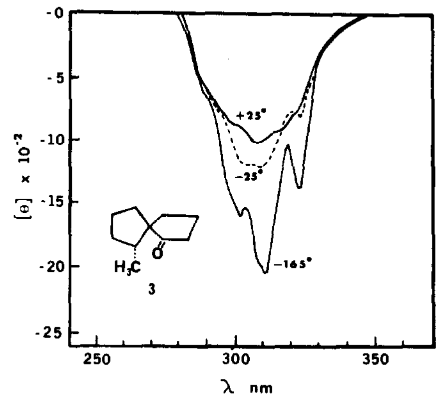
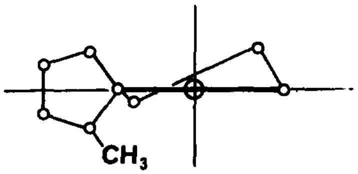
common precursor, (-)-6-methylidenespiro[4·4]nonan-1-one (4) derived from the known (-)-dione 5.[4,5,6] The temperature dependent circular dichroism (CD) spectra in methylcyclohexane-isopentane (1:5) of 2 and 3 are presented below. In both cases a (-) Cotton effect (CE) is found. The reduced rotational strengths for 2 and 3 are similar at +25°C (-1.0 and -1.2 respectively) but differ at -165°C (-2.8 and -1.7 respectively). Well-defined vibrational fine structure is



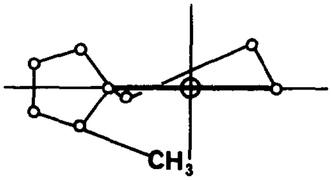


a striking feature of the CD spectrum of 2.

Although the optical rotatory dispersion and CD spectra of cyclopentanones appeared at first to contradict the signs and magnitudes of the CE predicted by the Octant Rule, it later became evident that any one or a combination of only three ring conformations (two half-chair and one envelope) frequently controlled the CE sign and determined its magnitude.[7] Inasmuch as the ring conformations of 5 have been shown in a recent x-ray study[8] to assume a form intermediate between half-chair and envelope (but closer to the former) and valence force calculations show it to be the most stable conformation,[8] we assume that this cyclopentanone conformation is the best and lowest energy model for 2 and 3. Thus, in octant diagrams[9] for the flattened half-chair cyclopentanone conformations shown in Dreiding models and based on the x-ray work on dione 5,[8] the *cis* methyl group of 2 lies either along side the carbonyl oxygen (a) or below and to the left of the midpoint of the C=O bond (b). Conformations (a) and (b) are obtained by holding the cyclopentanone ring fixed and flexing the cyclopentane ring. In both conformations (a) and (b) of 2 the cyclopentanone ring is shown in a flattened half-chair with ring carbon atom 3 lying in (-) back octants, ring carbon 4 nearly in a C=O symmetry plane, and the C-6 methyl group lying in a (+) front octant or in the third octant plane.[1-3] The more remote carbon atoms 6-9 are nearly symmetrically disposed about the second carbonyl local symmetry plane. They become effectively cancelled in a 50:50 mixture of (a) and (b) and therefore offer little or no sign-determining octant contributions. On the basis of the Octant Rule, one should anticipate, therefore, that both conformations (a) and (b) should give a net (-) CE due mainly to C-3 (and C-4), without yet adding in the methyl contributions. These contributions are predicted to be near zero in (b) and (+) in (a). Unless there is a large *magnitude associated with the front octant (+) contribution of (a)*, the net CE for 2 is expected to be negative, and this is observed.



(a)



(b)

On the other hand, the *trans* methyl perturber of ketone (3) is always in a (-) back octant. Thus the summed octant contributions of 3 predict the (-) CE which is observed. However, the preceding arguments also predict that the magnitude of the (-) CE associated with 3 will be greater than that of 2. While the rotational strengths are comparable at room temperature, at -165°C, the rotational strength of 2 is greater than that of 3. Without resorting to the selective inclusion of additional cyclopentanone conformers which bring in (+) octant contributions, the observed difference in rotational strengths of 2 and 3 at -165°C may be explained as follows. The *trans* methyl group of 3 can assume a configuration similar to that of the methyl group in 3-axial methylcyclohexanone which has been shown to give a very weak anti-octant contribution.[10] Although a (-) CE is still predicted for 3 based on the ring carbon octant contributions from the cyclopentanone ring [see (a) and (b) above], the magnitude is lessened. The *cis* methyl group of **2** has not yet reached into or beyond the third octant plane and therefore plays the the role of a (-)-back octant contributor to give **2** a more negative CE than **3**. These arguments require the third octant plane to be either very close to the oxygen of the C=0 group or to approximate a concave surface (as seen from oxygen toward carbon of the C=O bond).

Acknowledgement: We wish to thank the National Science Foundation (GP9355) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research (PRF 4949-ACS). We also thank Professor D. J. Cram for his advice and encouragement during the course of this work. The Cary 60 ORD-CD instrument used in this work was purchased with funds made available by the National Science Foundation (GP1682).

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