

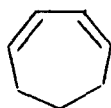
RING INVERSION IN EUCARVONE

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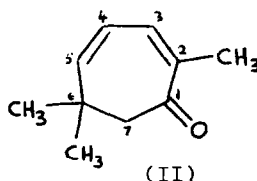
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Considerable attention¹ has been directed towards the determination of conformations and conformational mobilities of simple seven-membered carbocycles which are fully saturated or have one or three endocyclic double bonds. On the other hand, the corresponding unfused systems possessing two double bonds in the ring have received little attention, though molecular mechanics calculations² on cyclohepta-1,3-diene (I) indicate an extremely high degree of molecular mobility for this molecule.



(I)



(II)

We now report results from a variable-temperature ¹H n.m.r. study of the structurally related compound eucarvone (II), whose ambient temperature spectrum has been previously described.³

In CF₂Cl₂ at -60°C the 100 M Hz ¹H n.m.r. spectrum of (II) corresponds to rapid ring inversion, and comprises, in addition to olefinic resonances a singlet at 8.91 τ (6H) from the gem-dimethyl protons, a narrow multiplet (coupling to olefinic hydrogens) centred at 8.09 τ (3H) from the methyl on C-2, and a closely spaced doublet from the methylene protons at 7.37 τ (2H, J₅₇ ca 1 Hz). Below ca -80°C both the gem-dimethyl and methylene resonances are markedly broadened, and by -130°C one observes the "frozen" spectrum with distinct resonances 24.1 Hz apart arising from the non-equivalent methyl groups the diastereotopic methylene protons now exhibiting AB quartet structure with

$\nu_{AB} = 52.5$ Hz and $J_{AB} = 13.3$ Hz. From the doublet coalescence $T_c = -105^\circ\text{C}$ one obtains⁴ $\Delta G^\ddagger = 8.3 (\pm 0.2)$ Kcal./mole and for the methylene protons $T_c = -100^\circ\text{C}$ and $\Delta G^\ddagger = 8.3 (\pm 0.2)$ Kcal./mole.

Comparison of the barrier to ring inversion of (II) with that for cyclohepta-1,3-diene (I) itself⁶ cannot be made on a simple basis owing to factors including differing transannular interactions and the possibility of significant partial deconjugation⁷ of the carbonyl group with the diene system occurring during the ring inversion of (II).

We intend to carry out molecular mechanics calculations on eucarvone with a view to elucidating the details of its ring inversion process.

References

1. See, for example: W. Tochtermann, Fortschr. chem. Forsch., 1970, 15, 378; G. Borgen and J. Dale, Acta Chem. Scand., 1972, 26, 3593; M. St. Jacques and C. Vaziri, Canad. J. Chem., 1973, 51, 1192.
2. N.L. Allinger and J.T. Sprague, Tetrahedron, 1973, 29, 3811; see also: K. Hagen and M. Traetteberg, Acta Chem. Scand., 1972, 26, 3643 [electron diffraction study of (I)]; P. Crews, Chem. Commun., 1971, 583 [n.m.r. study of (I)].
3. A.A. Bothner-By and E. Moser, J. Amer. Chem. Soc., 1968, 90, 2347.
4. Calculated by employing $k = \pi\nu_{AB}/\sqrt{2}$ for the doublet coalescence and $k = \pi\sqrt{\nu_{AB}^2 + 6J_{AB}^2} / \sqrt{2}$ for the AB type coalescence (ref. 5). A mild temperature dependence in "frozen" shifts was taken in account by extrapolation.
5. M. Oki, H. Iwamura, and N. Hayakawa, Bull. Chem. Soc. Japan, 1964, 37, 1865.
6. Preliminary 100 M Hz ¹H n.m.r. measurements of the methylene resonances of (I) in the temperature range $+30^\circ$ to -130°C have shown no indication of kinetic effects.
7. The low $\nu(\text{C}=\text{O})$ of eucarvone, 1661.5 cm^{-1} in CCl_4 , indicates strong conjugation of the carbonyl group.