Tetrahedron Letters No.55, pp. 4833-4836, 1970. Pergamon Press. Printed in Great Britain.

NUCLEAR MAGNETIC RESONANCE STUDY OF RING INVERSION IN 1,3,5 - CYCLOOCTATRIENE

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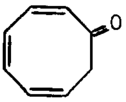
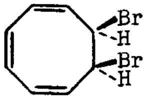
(Received in USA 21 October 1970; received in UK for publication 2 November 1970)

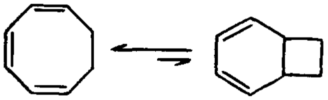
The energy barriers to ring inversion of 3,5,7-cyclooctatrienone (I) (1), and cis-1,2-dibromo-3,5,7-cyclooctatriene (II) (2) have been determined by proton magnetic resonance (pmr) spectroscopy. We wish to report that the parent compound, 1,3,5-cyclooctatriene (III)*, has an appreciably lower inversion barrier.



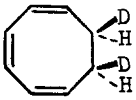
I



II



III IV



V

The 100 MHz pmr spectrum of III at 24°C consists of a narrow multiplet (four protons) centered at 2.43 ppm downfield from internal TMS assigned to the methylene protons on C(7) and C(8) and two slightly overlapping multiplets centered at 5.71 ppm and 5.88 ppm attributed to the six olefinic protons. Figure 1a shows that the 2.43 ppm multiplet changes as the temperature is lowered such that at -161°C a rather complex pattern is observed. Since this multiplet is part of a ten spin system, it is not possible to calculate the kinetic parameters for the ring inversion from the spectral change.

* The cyclooctatriene was purified as described by Cope and co-workers (3). Pmr spectra were recorded on a JEOL JNM-4H-100 spectrometer equiped with variable temperature accessories and an heteronuclear decoupling unit. Temperatures are accurate to within ± 2°C.

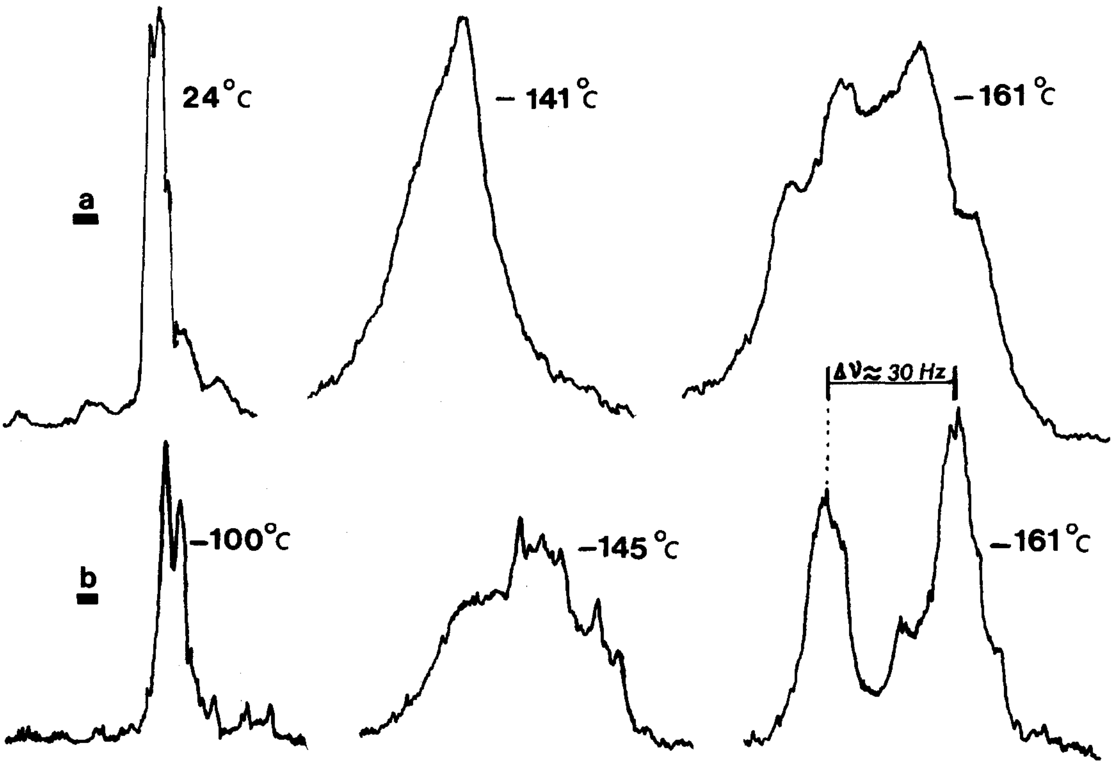
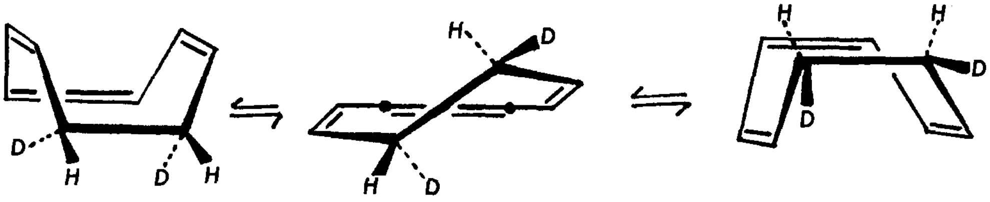


Figure 1. a) 100 MHz pmr spectra of the upfield multiplet of III at several temperatures using a 10% solution in chlorodifluoromethane. b) 100 MHz deuterium decoupled pmr spectra of V at several temperatures using a 5% solution in a mixture of CHF_2Cl and $CH_2 = CHCl$ (1:1).

To simplify the low temperature spectrum cis-7,8-dideuteriocyclooctatriene (V) was prepared from the partial reduction of cyclooctatetraene with deuterium and tris(triphenylphosphine)chlororhodium (4). The pmr spectrum of this compound closely resembles that of III with the exception that on deuterium decoupling the upfield peak (2.41 ppm) is a doublet (separation = 3.1 hz). Figure 1b shows its behaviour as the temperature is lowered. Treating the spectral change as being due to a two site exchange (inside and outside protons in the boat form shown below) it is possible to obtain a reasonable estimate of the free energy barrier to ring inversion. From the relationship $k = \pi \Delta\nu/\sqrt{2}$ (5) and the Eyring equation, $\Delta F^{\dagger}$ is calculated to be 6.2±0.5 kcal/mole at -145°C, the coalescence temperature. The error for $\Delta F^{\ddagger}$ is estimated by considering the uncertainties in T_c (± 3°C), $\Delta\nu$ (± 2Hz) and the approximate nature of the calculation.

The valence tautomerism between III and IV has recently been studied (6). It is reported that at equilibrium at 60°C there exists about 10.8% of IV and that the equilibrium between these two tautomers is established slowly ($\Delta H^{\ddagger}$ = 26.6 kcal/mole, $\Delta S^{\ddagger}$ = -1 e.u.). This equilibrium should then have no effect on the rate of ring inversion of pure III (or **V**) determined by pmr below -100°C.

The lowest energy conformation of V is undoubtedly a member of the boat family as has been suggested for I (1) and II (2). A possible mechanism for the interconversion of boat forms is shown below where the transition state is suggested by Fieser models; it possesses a two-fold axis of symmetry through the C(3) —— C(4) and C(7) —— C(8) bonds which implies an eclipsed arrangement about the C(7) — C(8) bond and near coplanarity of the three double bonds.



POSSIBLE TRANSITION
STATE

Table I lists the energy barriers for inversion in compounds I, II, V as well as for the conformationally related cyclooctatetraene (VI) (7) and fluorocyclooctatetraene (VII) (8).

TABLE I

Free energies of activation of cyclooctatetraenes and cyclooctatrienes.

Compound	$\Delta F^{\ddagger}$ kcal/mole	Ref.
Cyclooctatetraene (VI)	13.7	7
Fluorocyclooctatetraene (VII)	12	8
I	11.9^a	1
II	13	2
V	6.2	this work

[a] This value is for the energy of activation obtained from an Arrhenius plot.

It is observed that I, II, VI and VII have very similar inversion barriers whereas that of V is much lower than all of them. Arguments based on torsional and angular strain suggest that the energy required to reach the strained planar transition state for the interconversion of cyclooctatetraene (7,8) should be greater than that required to reach the less strained transition state proposed for V in accord with the observed $\Delta F^{\ddagger}$ values. But since an inversion mechanism similar to that of V has been suggested for I and II (1), the much lower $\Delta F^{\ddagger}$ value estimated for the parent 1,3,5-cyclooctatriene reflects a structural dependence of the relative stabilities of the boat conformations and the transition states for these compounds.

We are planning to obtain more experimental results from a study of structural effects on the barrier to ring inversion of other cyclooctatriene derivatives.

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