RESEARCH THESIS

FOR CHEMISTRY 80

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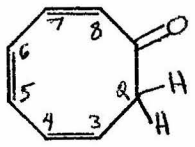
RING INVERSION IN 3,5,7-CYCLOOCTATRIENONE

The temperature dependence of the proton nmr spectrum of 3,5,7-cyclooctatrienone (I) was studied with the aid of a Varian Model HR-60 spectrometer equipped with a special low-temperature probe using a 25% by volume solution of I in carbon disulfide with tetramethysilane (TMS) as internal standard.

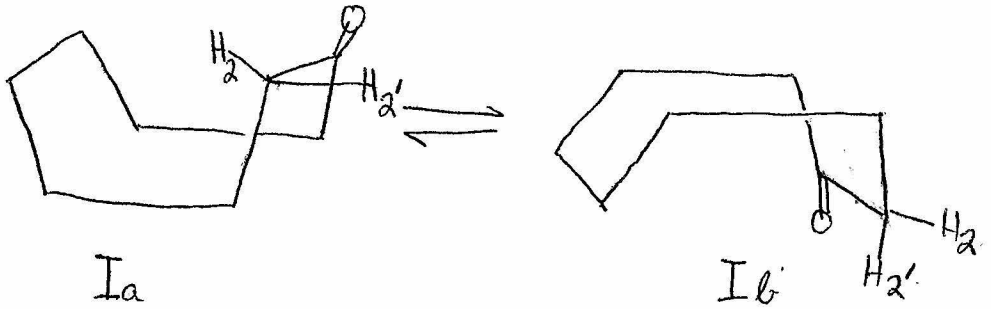
The nmr spectrum of I at 35° (Figure 1) shows a multiplet centered around 390 cps (TMS = 0 cps) which can be attributed to the resonance of the vinylic protons, H_5 through H_7. The downfield side of this multiplet is most likely the resonance of H_8 since this proton is alpha to the carbonyl group which is more electronegative than the carbon-carbon double bond (Figure 1).



I

The resonance of H_3 is a sextet centered around 340 cps which is upfield of the other vinyl peaks due to the shielding by the two 2-position protons. The H_3 signal is split into a doublet by H_4 with J_{3-4} = 10 cps, each peak of which is in turn split into a triplet by the two 2-position protons with J_{2-3} = 8 cps (Figure 1).

If the inversion between Ia and Ic were slow on the nmr time scale, then there would be two separate resonances due to



Ia Ib

the different magnetic environments of the two 2-position protons: one for the axial proton (H_2 in Ia or $H_{2'}$ in Ib) and one for the equatorial proton ($H_{2'}$ in Ia or H_2 in Ib). But in reality the molecule flips fast enough at room temperature to average the axial and equatorial resonances, yielding a mean chemical shift of 180 cps downfield of TMS. This average spectrum shows a doublet with an 8 cps splitting due to the coupling with H_3 (Figure 1). This interpretation of the spectrum is upheld by the integration of the peaks.

At temperatures above -20°, the rate of inversion is sufficiently rapid that only a doublet resonance is observed for the two C(2) protons (Figure 1a). This doublet corresponds roughly to the AB part of an ABX spectrum (A = H(2endo), B = H(2exo), X = H(3)) with $\delta_{AB} \sim 0$ as would be expected for interchange of the magnetic environments of the C(2) protons by ring inversion as shown in Ia-Ib. As the temperature is lowered, the doublet coalesces and at -43 to -44° a broad singlet is observed. At still lower temperatures, the signal of the protons at C(2) sharpens to take the appearance of the AB part of an ABX spectrum with $\Delta\nu_{AB} \sim 25$ cps (Figure 1b). No further change occurs below -80°.

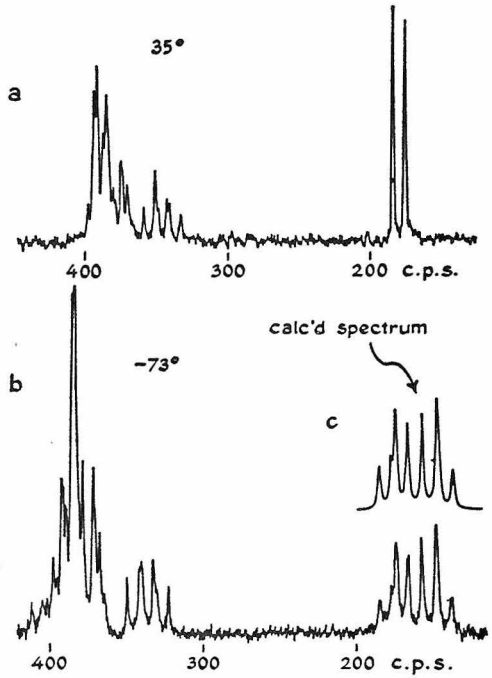


Figure 1. (a) Observed spectrum of 3,5,7-cyclooctatrienone at 35°, (b) observed spectrum of 3,5,7-cyclooctatrienone at −73°, and (c) calculated AB part of frozen-out ABX spectrum.

protons) between δ 6.1 and 6.6 assigned to the protons on C(4) through C(8)

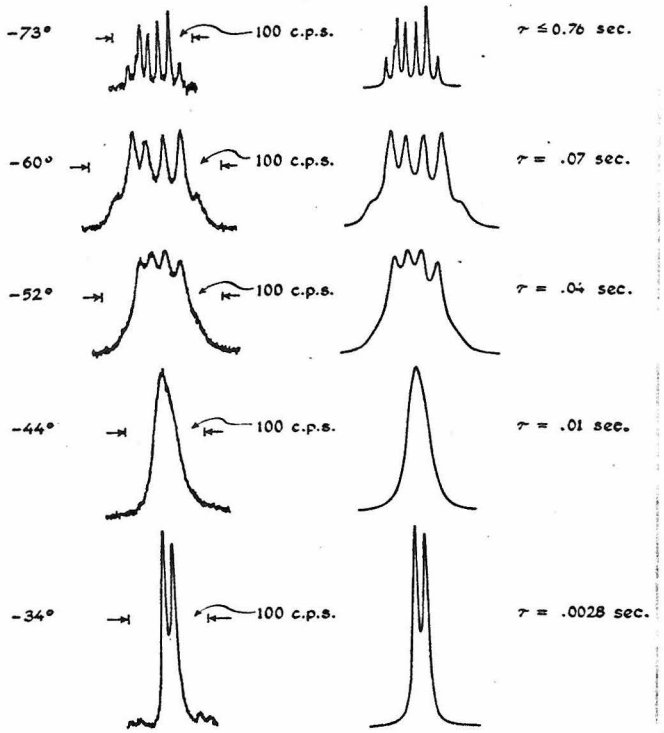


Figure 2. Observed (left) and calculated (right) spectra of the AB part [H(2n), H(2x)] of 3,5,7-cyclooctatrienone as a function of τ.

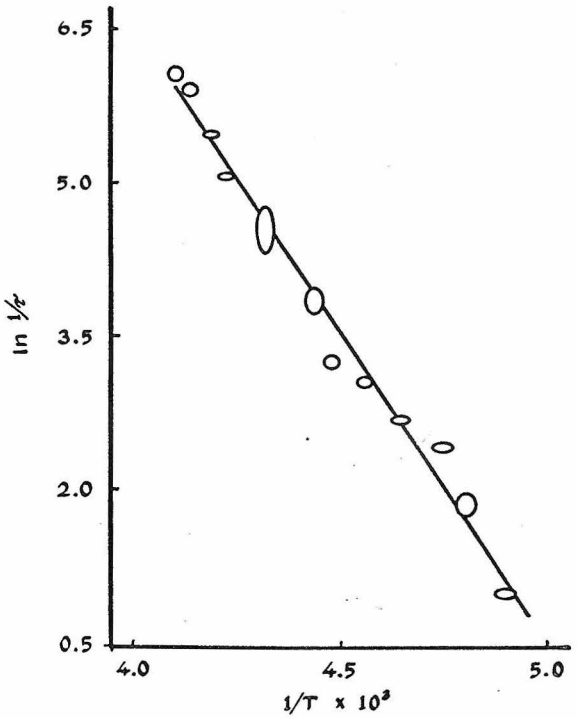


Figure 3. Arrhenius plot for inversion process. The points ar shaped to accord with the estimated uncertainties in temperatu or in matching curves to obtain τ.

The three-spin ABX-type system with slow inversion was analyzed with the aid of the computer program developed by Ferguson[1] on the assumption that the effect of the coupling between the X proton on C(3) and the protons on C(4) through C(8) could be neglected for the AB part of the spectrum. The parameters which gave good agreement for the AB part of the spectrum were v(2endo) = 165.4, v(2exo) = 190.7, v(3) = 344.0, J(2endo, 2exo) = -10.0, J(2endo, 3) = 9.0, and J(2exo, 3) = 7.2 (all values in cps with chemical shifts from TMS as internal standard). The observed and calculated spectra with these parameters are compared in Figures 1b and 1c.

Trial calculated spectra with J(2endo, 8) and J(2exo, 8) assigned values from 0 to 1 cps, J(2endo, 4) from 0 to -1.7 cps, and J(2exo, 4) from 0.2 to 1.1 cps[2] showed no significant changes in the AB part of the spectrum other than small broadening effects.

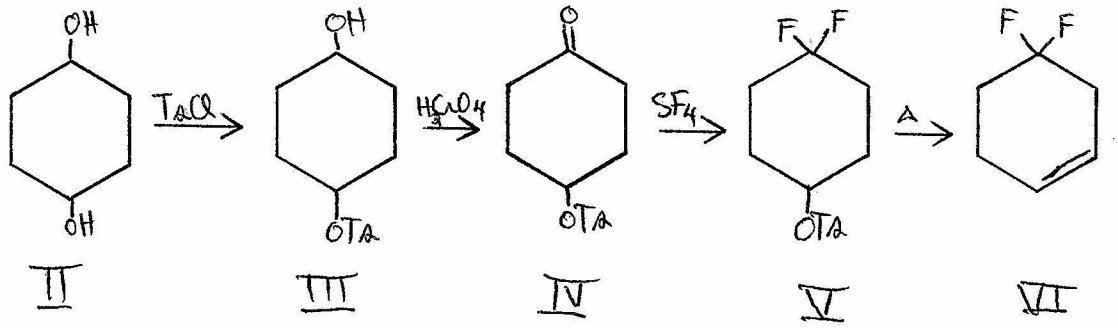
The assignment of the endo proton H(2) in Ia giving resonance at higher field than the exo proton H(2') in Ia is based on an expected substantial shielding effect of the C(3)-C(4) double bond. Such an effect has been observed for cis-1,2-dibromo-3,5,7-cyclooctatriene.[3]

Spectra were taken from -85 to +35° in order to evaluate the activation energy, E_a, for ring inversion. The rate of inversion at each temperature was determined with the aid of calculated theoretical spectra having various values of the mean half-life (tau) calculated by means of a Fortran IV coded program.[4] In each case, tau was adjusted until the theoretical spectra

were as nearly superimposable as possible on the observed spectra. Representative observed and calculated spectra are shown in Figure 2. An activation energy of E_a = 11.9 ± 0.5 kcal/mole for the inversion process was obtained from a least-squares fit to the Arrhenius plot of Figure 3. It is interesting to compare this value with energies for bond shift in cyclooctatetraene (13.7 kcal)[5] and fluorocyclooctatetraene (ca.12 kcal for free energy of activation)[6] and for inversion in cyclooctatetraenyl-dimethylcarbinol (14.7 kcal)[5] and cis-1,2-dibromo-3,5,7-cycloocta-triene (13 kcal for free energy of activation)[3].

SYNTHESIS OF 1,1-DIFLUORO-3-CYCLOHEXENE

In order to undertake a similar nmr study, 1,1-difluoro-3-cyclohexene (VI) was synthesized in the following manner. 1,4-cyclohexanediol (II) was reacted with tosyl chloride (para-toluene sulfonyl chloride) to yield 1,4-cyclohexanediol monotosylate (III).



III was then oxidized with chromic acid to give the ketone (IV). IV was fluorinated with gaseous sulfur tetrafluoride to the gem-difluoride (V). Finally, the tosyl group was eliminated by distillation at high temperature to yield the product (VI).

Experimental:

Tosylation: Sixteen grams of toluene-p-sulfonyl chloride in 65ml of chloroform at 5° were added with stirring within two hours to 10g of II in 55ml of pyridine. The solution was allowed to sit overnight at room temperature. The worked-up product was dissolved in 30ml of diethyl ether.

Oxidation: Fifty ml of an aqueous chromic acid solution

prepared with 8.64g of sodium dichromate dihydrate and 6.50ml of concentrated sulfuric acid, the theoretical quantity of oxidant for 16g of III, were added with stirring within one hour to the above solution of the crude tosylation product at 2°. The mixture was stirred for another hour at 2° and then extracted with diethyl ether and washed with water. Evaporation of the ether left about 10g of crude product.

Fluorination: Five grams of the crude oxidation product dissolved in 25ml of methylene chloride and 1ml of water were shaken overnight at room temperature in a pressure vessel containing 40g of sulfur tetrafluoride gas. The product was washed with an aqueous sodium bicarbonate solution and the solvent evaporated.

Tosyl Removal: One gram of the fluorination product was distilled at atmospheric pressure yielding several drops of a pungent-smelling, colorless liquid boiling at 75°, identified by nmr and comparison with the spectrum of cyclohexene.

REFERENCES

(1) R.C.Ferguson and D.M.Marquardt, J.Chem.Phys., 41, 2087(1964)

(2) These signs and values for the allylic coupling constants, J(2endo,4) and J(2exo,4), were chosen in accordance with dihedral angles estimated from models using the theoretical treatment of long-range proton spin-spin coupling across four bonds in unsaturated hydrocarbons proposed by M.Barfield, ibid, 3825(1964)

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(4) R.A.Newmark and C.H.Sederholm, J.Chem.Phys, 43, 602(1965). This program was adapted for our use by Dr.J.T.C.Gerig.

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(6) D.E.Gwynn, G.M.Whitesides, and J.DRoberts, ibid, 87, 2862(1965)