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MICROWAVE AND NMR STUDIES OF THE STRUCTURE AND THE CONFORMATIONAL ISOMERIZATION OF 3,6-DIHYDRO-1,2-DIOXIN

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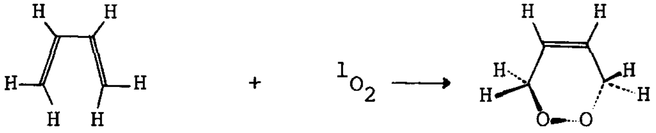
Structures of fundamental organic peroxides such as 1,2,4-trioxolanes[1], peracetic acid[2], and dioxirane[3] have been well established by microwave spectroscopy. 3,6-Dihydro-1,2-dioxins (1,4-endoperoxides) are also fascinating peroxides which are easily obtained by the reaction of 1,3-dienes with singlet oxygen[4] and are utilized as versatile intermediates in organic syntheses.[5] No data, however, are available concerning the molecular structure and the conformational isomerization of the simplest 1,4-endoperoxide. We have established the conformation of the 3,6-dihydro-1,2-dioxin (1) by means of microwave and nmr spectroscopy.

The peroxide 1 was prepared by a photosensitized oxygenation of 1,3-butadiene.[6] A solution of 1,3-butadiene and Rose Bengal (sensitizer) in tetraethyleneglycol dimethyl ether was irradiated with a 500-W halogen lamp for 15 h at 0°C under an oxygen atmosphere. The peroxide 1 was obtained as a colorless liquid (bp 108°C) in a yield of 20%.



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The microwave spectrum was observed with a conventional 110-kHz Stark-modulated spectrometer. The measurement was carried out at dry-ice temperature, unless otherwise indicated. We observed b-type Q-branch transitions of low J, and the values of (A - C)/2 and κ were determined by the use of a Q-branch plot[7]. The value of (A + C)/2 was obtained by the observation of R-branch lines of low J. The assignment of spectral lines was confirmed by the characteristic Stark patterns, as well as by the agreement with the frequencies calculated for a half-chair model using suitable values of molecular parameters. The half-chair conformation is attributed to this molecule by substantial evidence described below. The b-type transitions with J less than 8 were observed in the frequency range from 8 to 26 GHz but no a- and c-type transitions were detected. Table I lists the rotational constants determined by a least-squares fit to the frequencies of transitions with J less than 4, together with the dipole moment obtained by Stark effect measurements on the several low-J transitions.

Table I. Rotational Constants[a)] (MHz) and Dipole Moment[a)] (D) of 3,6-Dihydro-1,2-dioxin

A	B	C
5287.43 ± 0.16	5110.21 ± 0.16	2857.85 ± 0.08
$\mu_{total} = \mu_b = 2.329 \pm 0.003$		

a) Errors are 2.5 times the standard deviations.

The correct conformation of 1 was first indicated by the observation of alternation in the intensities of transitions from rotational levels of opposite symmetry. This alternation in intensity arises in 1 only if a C_2 rotational symmetry axis is present in the molecule; therefore, the molecule cannot have a boat conformation which belongs to the C_s symmetry. The observed ratio of the intensity of $4_{23} - 4_{14}$ (antisymmetric transition; $\nu_0 = 16369.5$ MHz, $\lambda_b = 0.9404$) to that of $4_{13} - 4_{04}$ (symmetric transition; $\nu_0 = 16367.0$ MHz, $\lambda_b = 0.9405$) was 1.30 ± 0.10 , if all other intensity factors of both transitions were considered to be the same. It is consistent with the ratio 9/7 which is expected for a molecule with three pairs of equivalent hydrogen nuclei with nuclear spin of 1/2. This result supports the half-chair model and puts the boat conformation out of consideration.

Kinetic parameters for the conformational isomerization of 1 were determined by the use of nmr spectroscopy. The high resolution nmr spectra of about 10% solution of 1 in CD_2Cl_2 were recorded on Varian Model XL-100A spectrometer in the temperature range from 25 to -100 °C. Because of the presence of a proton coupling, the resonance lines of the gem-hydrogen of methylene groups are particularly complicated. At room temperature they appear as a single sharp line (δ 4.56) which broadens as the temperature is lowered until -69.4°C where the coalescence temperature is reached. Below the coalescence temperature the spectrum exhibits resolution first into a diffuse doublet and finally (-96°C) into a distinct quartet of a coupled AB system. The exchange rate was calculated from a computer-assisted simulation by a complete line-shape method using the density matrix equations in the form given for a coupled AB case.[8] The spin-spin coupling constant and the chemical shift between the methylene protons in the nmr spectra of 1 in CD_2Cl_2 at -96°C are 16.0 and 56.0 Hz, respectively. The transverse relaxation time is determined by the linewidth of the sharp single line in the spectrum measured at room temperature ($T_2 = 0.14$ s). An Arrhenius plot of the rate constants thus obtained permitted the determination of activation energy by a least-squares fit, and the Eyring formulation was used to calculate the thermodynamic parameters for the transition state. The results are compared with those for 3,3,5-trimethyl-3,6-dihydro-1,2-dioxin[9] (2) in Table II. The opposite signs in the entropy of activation clearly show that the conformational isomerization of 1 follows a reaction pathway different from that proposed for 2[9]. The negative entropy of activation obtained for 1 suggests that the activated complex

Table II. Transition State Parameters for Half-Chair Inversion of 3,6-Dihydro-1,2-dioxin and 3,3,5-Trimethyl-3,6-dihydro-1,2-dioxin

	K		kcal/mol			eu	
	T_c a)	$\log A$ b)	E_a c)	$\Delta G^{\ddagger}_{cc}$ d)	$\Delta H^{\ddagger}_{cc}$ e)	$\Delta S^{\ddagger}_{cc}$ f)	Ref.
3,6-Dihydro-1,2-dioxin	203.8	11.9	9.0	9.7	8.6	-5.4	this work
3,3,5-Trimethyl-3,6-dihydro-1,2-dioxin	214.7		13.0	11.0	12.6	7.4	9

a) coalescence temperature b) A: frequency factor c) activation energy
d) obtained from the rate constant at T_c e) obtained from the equation of $\Delta H^{\ddagger}_{cc} = E_a - RT_c$ f) obtained from the equation of $\Delta S^{\ddagger}_{cc} = (\Delta H^{\ddagger}_{cc} - \Delta G^{\ddagger}_{cc})/T_c$

possesses a greater degree of order (a rigid, planar or near-planar form) than the starting half-chair form.

The rotational constants shown in Table I resulted in the C-C=C, C-C-O, and twist angles to be 119.9, 110.3, 38.3°,respectively, on the assumption that the C=C, C-C, C-O, C-H (olefinic), and C-H (methylene) bond distances were to be 1.338, 1.504, 1.426, 1.09, and 1.10 Å, respectively. Following plausible assumptions were also introduced in this calculation: (1) the four carbon atoms are in a plane, (2) the olefinic hydrogen atom lies on the bisector of the adjacent ring angle C-C=C, (3) H-C-H angle is equal to the tetrahedral angle 109°28', sharing a common bisector with the adjacent ring angle C-C-O, (4) all C-C-H angles associated with methylene groups are equal. The C-C=C angle thus obtained is found to be narrower than those in cyclohexene (123.3°)[10], and 3,6-dihydro-2H-pyran (122.2°)[11]. It may be resulted in by the fact that the O-O distance 1.463 Å is shorter than a normal C-C distance in six-membered ring molecules containing a C=C ring bond. The twist angle between the O-O bond and the plane involving the four carbon atoms is larger than in cyclohexene (30.1°)[10] and 3,6-dihydro-2H-pyran (31.5°)[11]. The details of the structural analysis will be reported elsewhere.

The absorption intensity of the transitions of 1 was found to decrease gradually at room temperature and, at the same time, new spectral lines appeared. The latter lines were assigned to the transitions of furan[12,13] and *s-trans*-acrolein[14,15]. In the case of the decomposition of 1 to acrolein (propenal), formaldehyde would be formed. However, no spectral lines of formaldehyde[16] could be observed in the spectrum, nor those of 1,3,5-trioxane[17], a trimer of formaldehyde. The amounts of furan and acrolein thus formed were estimated from the relative intensities of the respective absorption lines using their calculated maximum absorption coefficients[18]. Furan was found to be formed 50-100 times as much as acrolein. Thus the peroxide 1 selectively decomposes into furan.

The peroxide 1 was found to have the lifetime of 15 min under the pressure of 20 mTorr in a red-brass waveguide cell at room temperature, whereas it is scarcely changed in a Pyrex tube at room temperature after a week.[19] The decomposition in the waveguide cell can be considered to be not a homogeneous thermal reaction but a heterogeneous catalytic reaction. We found that cuprous chloride is more effective than metallic copper and cupric oxide to convert 1 selectively into furan in gas phase.[20]

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(19) The gaseous peroxide 1 decomposes to produce furan in a Pyrex tube at about 210°C within 10 h.

(20) Ferrous sulfate has been known to enhance catalytically the furan formation from the 1,4-endoperoxides.[5d]

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