THE GEOMETRICAL STRUCTURES OF THE SUBSTITUTED OXIRANES.

COMMUNICATION 6. THE STRUCTURES OF THE OXIRANECARBALDEHYDES

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Information on internal rotation around the bond joining the oxirane ring and the C=O group in the oxiranecarbaldehyde molecule is limited to several NMR studied which are consistent as to the results obtained, but differ in the way in which these results have been interpreted. Thus, while it has been suggested [1] that the curve showing the variation of the internal energy in the glycidyl aldehyde molecule must pass through three minima, just as in the case of vinylcyclopropane, it has also been claimed [2] that there is only a twofold barrier to rotation in this molecule, just as in cyclopropanecarbaldehyde. Drawing on the data

Fig. 1. NMR spectra of compounds (I) and (II).
of [5], the authors of [3, 4] conclude that this latter compound exists largely, if not exclusively, as a conformer with dihedral angle close to either 0° or 180°. Our own studies [6] have shown that the energy curve for internal rotation in the acetyloxirane molecule passes through two minima. An increase in the size of the substituent at the C=O bond (R = t-Bu) forces the molecule into a single type conformation. Conformational equilibria are established in systems containing smaller substituents (R = Ph, Me), the conformer ratio changing as the size of the substituent at the C=O bond is altered. In testing these points, it is necessary to study the geometrical structures of compounds in which the substituent at this bond is small enough so that steric hindrances can be neglected. Considerable interest attaches to a comparison of the structures of the oxiranecarbaldehydes, on the one hand, and the acetyloxiranes, on the other. It is known that there are differences in the geometrical structures of these two classes of compounds, the aldehydes existing as essentially 1:1 equilibrium mixtures of s-cis and s-trans forms, and the propanes as equilibrium mixtures of these same forms but with the point of equilibrium shifted almost completely to the s-cis side [7-11].

The geometrical structures of the oxiranecarbaldehydes were determined through the study of compounds of the following type:

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\text{R} = \text{Me (I), Ph (II)}
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A study was made through IR and PMR spectroscopy and through measurement of dipole moments (DM) and Kerr constants. Molecular configurations were determined through PMR methods. The spectra of the compounds in question here are shown in Fig. 1. The fact that the spin-spin coupling constant (J) for the oxide ring had the value 2Hz indicated that each of these molecules existed in the trans-configuration [12].

The existence of conformational equilibria in similarly structured compounds has been demonstrated by the appearance of a doublet carbonyl absorption band in the IR spectra [13, 14]. Measurement showed that the IR spectra of (I) and (II) each contained a single absorption band in the ν C=O region, the position of this band varying with the dielectric constant of the solvent: (I) 1732 (CCl₄), 1728 (CH₃CN) and 1727 (liquid); (II) 1708 (CCl₄), 1702 (CH₃CN) and 1701 cm⁻¹ (liquid). The fact that Jvic for the aldehyde proton and the proton at the oxide ring remained constant at 6Hz as the temperature was varied from -100 to +60°C was taken as indication that conformational equilibria were not established in these systems, at least not to a degree detectable by the methods used here.

Use was made of the geometrical parameters of the oxirane ring and the bond and group dipole moments and polarizability parameters given in [6] in calculating the dipole moments