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Intramolecular Interaction between the Hydroxyl Group and the Oxirane Ring[1]

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The intramolecular interaction between the hydroxyl group and the oxirane ring has been detected by means of studying the infrared spectra in the 3μ region of various hydroxyalkyloxiranes. The O–H stretching absorptions of several compounds which have limiting structures in the sence of the conformational preference have been closely examined. The results indicate that the intramolecular interaction takes place between the hydroxyl group and the electron orbitals involved in the formation of the C–O bond, while that involving the electrons of the C–C bond can be neglected.

It has been established that the cyclopropane ring interacts with the hydroxyl group, the former acting as a proton acceptor.[2] This property of the cyclopropane ring is, of course, attributable to the strain of the bonds or to the low ionization potential of the electrons. Since the oxirane ring is an oxygen analog of the cyclopropane, it can naturally be expected that the oxirane ring will behave similarly; the study of the intramolecular interaction between the hydroxyl group and the oxirane ring is thus undertaken as an extension of the previous work.

Since the oxirane ring contains an oxygen atom, the three bent bonds of the ring, namely one C–C and two C–O bonds, are not equal. Because of the high electronegativity of the oxygen atom, oxirane has been reported to have a dipole moment (1.91 D)[3] which is slightly larger than those of tetrahydrofuran (1.63 D)[3] or dimethyl ether (1.29 D).[4] Thus, the electron densities of the bent bonds of the ring are clearly not equal, that of the C–C bond being tenuous.[5] It may be postulated, therefore, that the electron orbitals involved in the C–O bond formation, rather than the C–C bond of the oxirane ring, will interact with the hydroxyl group, if any O–H···oxirane interaction does exist.

This paper will deal with the detection of such an intramolecular interaction and with the dynamic stereochemistry which is necessary in establishing the interaction in detail. It will also seek to determine if the above expectation as to the site of the interaction is really correct.

Experimental

Spectral Measurements. The infrared absorption spectra in the 3μ region were measured on a Perkin-Elmer 112G single-beam grating spectrophotometer, the slit width being 0.8 cm^{-1} in this region. The apparent absorption curves were graphically separated into symmetrical curves.

Wako special-grade carbon tetrachloride was used in making up the solutions of alcohols. The concentrations of the solutions were *ca.* 0.003 mol/l. A quartz optical cell 2 cm thick was used.

The NMR spectra were taken on a JNM 3H-60 spectrometer.

Materials. All the alcohols except *erythro*-3,4-epoxy-4-methylpentan-2-ol (VIII) were prepared by the epoxidation of the appropriate unsaturated alcohols with perbenzoic acid. The acids were removed with calcium hydroxide during the reaction in order to avoid isomerization as much as possible.[6]

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[1] A preliminary report has been published: M. Ōki and T. Murayama, This Bulletin, **40**, 1997 (1967).

[2] (a) L. Joris, P. von R. Schleyer, and R. Gleiter, *J. Amer. Chem. Soc.*, **90**, 327 (1968); (b) M. Ōki, H. Iwamura, T. Murayama, and I. Oka, This Bulletin, **42**, 1986 (1969); (c) Z. Yoshida, N. Ishiba, and H. Kusumoto, *J. Amer. Chem. Soc.*, **91**, 2279 (1969).

[3] W. L. G. Gent, *J. Chem. Soc.*, **1957**, 58.

[4] G. A. Barclay and R. J. W. Le Fèvre, *ibid.*, **1952**, 1643.

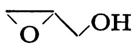
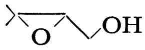
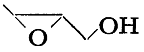
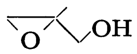
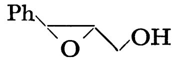
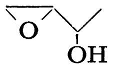
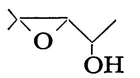
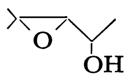
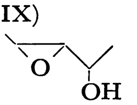
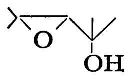
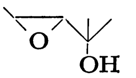
[5] A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).

[6] H. B. Hebest and B. Nicholls, *J. Chem. Soc.*, **1959**, 221.

The epoxidation of 4-methyl-3-penten-2-ol gave *threo*-3,4-epoxy-4-methylpentan-2-ol (VII); bp 67—68°C/15 mmHg, $n_{\rm D}^{16.5}$ 1.4270. This compound was identical with the one obtained by the isomerization of *cis*-2-methyl-3,4-epoxypentan-2-ol.[7] (lit. bp 75—76°C/20 mmHg, $n_{\rm D}^{25}$ 1.4238). NMR (δ from TMS in CCl_4): 1.15 (3H, d, J=6 Hz), 1.26 (3H, s), 1.27 (3H, s), 3.20—2.80 (1H, m), 2.62 (1H, d, J=8 Hz), 4.10 (OH).

erythro-3,4-Epoxy-4-methylpentan-2-ol (VIII) (bp. 68.5—69°C/10 mmHg, $n_{\rm D}^{16.5}$ 1.4271) was obtained by the isomerization of *trans*-2-methyl-3,4-epoxypentan-2-ol.[7] NMR (δ from TMS in CCl_4): 1.25 (3H, d, J=6 Hz), 1.30 (6H, s), 2.48 (1H, d, J=8.5 Hz), 3.48 (1H, m), 3.81 (OH).

TABLE 1. $\nu_{\rm O-H}$ DATA OF EPOXY ALCOHOLS

Compound	$\nu_{\rm max}$ (cm^{-1})	$A\times10^{-3}$[a] (mol·l·cm)	Relative intensity
2,3-Epoxypropan-1-ol (Glycidol) (I) 	3638 3611.8 3590	0.21 2.9 3.1	1 14 15
2,3-Epoxy-3-methylbutan-1-ol (II) 	3638 3612.4	1.6 4.0	1 2.5
trans-2,3-Epoxybutan-1-ol (III) 	3638 3610.0 3583	0.62 2.8 4.0	1 4.5 6.4
2,3-Epoxy-2-methylpropan-1-ol (IV) 	3639 3609 3578.1	0.29 2.1 4.2	1 7.5 15
trans-2,3-Epoxy-3-phenylpropan-1-ol (V) 	3637 3611.2 3590	0.28 4.6 3.1	1 17 11
3,4-Epoxybutan-2-ol (VI) 	3607.0 3573	2.6 2.7	1 1
threo-3,4-Epoxy-4-methylpentan-2-ol (VII) 	3628 3607.4	0.27 5.0	1 19
erythro-3,4-Epoxy-4-methylpentan-2-ol (VIII) 	3623.6 3612 3567	4.8 0.2 1.7	1 0.04 0.37
trans-3,4-Epoxypentan-2-ol (IX) 	3624 3606.1 3569	0.41 3.4 3.3	1 8.3 7.9
3,4-Epoxy-2,4-dimethylpentan-2-ol (X) 	3617 3559.4	0.6 8.2	1 13.3
trans-3,4-Epoxy-2-methylpentan-2-ol (XI) 	3598 3566.4	0.5 4.6	1 9.2

a) "A" denotes the integrated intensity of the band.

Results and Discussion

The spectral data of the O–H stretching absorptions ($\nu_{\rm O-H}$) of several 2,3-epoxypropan-1-ol derivatives are given in Table 1. Some representative curves are also given in Fig. 1.

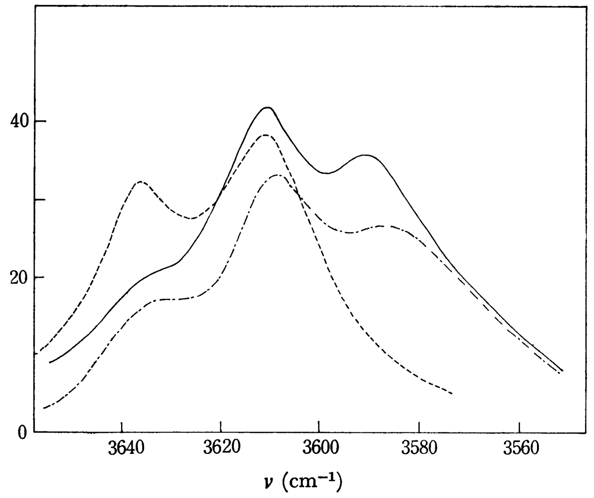


Fig. 1. $\nu_{\rm O-H}$ absorption bands of 2,3-epoxypropan-1-ol (I: ——), 2,3-epoxy-3-methylbutan-1-ol (II: ------), and *trans*-2,3-epoxybutan-1-ol (III: —·—).

The $\nu_{\rm O-H}$ curve of glycidol (I) apparently has three absorption peaks. One of the three maxima can certainly be assigned to the hydroxyl group which is hydrogen-bonded to the oxygen atom of the oxirane ring. In order to establish this assignment, the $\nu_{\rm O-H}$ absorptions of several alcohols with a similar situation have been measured: tetrahydrofurfuryl alcohol and 2-hydroxymethyloxane[8] show their O–H···O bonded $\nu_{\rm O-H}$ at 3602 and 3597 cm^{-1} respectively. It is then found that the band at the lowest frequency, 3590 cm^{-1}, is most probably the intramolecularly O–H···O-bonded band. The band at the highest wave number, 3638 cm^{-1}, can be assigned to the free OH group of the primary alcohol, because other primary alcohols are known to give rise to an absorption at *ca.* 3636 cm^{-1} [9]

TABLE 2. $\nu_{\rm O-H}$ DATA OF RCH_2OH

R	$\nu_{\rm max}$ (cm^{-1})	$A\times10^{-3}$ (mol^{-1} l cm^{-2})	A_l/A_h[a]	Ref.
CH_3	3637.3 3627	2.8 1.6	0.56	9
$(CH_3)_2CH$	3641.5 3628	3.6 1.8	0.50	9
	3633.7 3619	2.3 2.6	1.1	2b

a) A_l and A_h denote integrated intensities of the bands at lower and higher frequencies, respectively.

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[7] C. B. Payne, *J. Org. Chem.*, **27**, 3819 (1962).

[8] S. A. Barker, J. S. Brimacombe, A. B. Foster, D. H. Whiffen, and G. Zweifel, *Tetrahedron*, **7**, 10 (1959).

[9] M. Ōki and H. Iwamura, This Bulletin, **32**, 950 (1959).

(see Table 2). The third band, 3611.8 cm^{-1}, is located at too low a frequency to be assigned to a second rotamer of the primary alcohol, which usually gives the absorption near 3625 cm^{-1} and which is located at a lower frequency than the intramolecularly O–H··· cyclopropane interacting band (see Table 2). Thus, the last band is attributable to the O–H···oxirane interacting species.

2,3-Epoxy-3-methylbutan-1-ol (II), which carries two methyl groups at the C_3 of the ring, failed to show absorptions below 3600 cm^{-1}. However, when we removed the methyl group at C_3 which is *cis* to the hydroxymethyl group, the absorption band below 3600 cm^{-1} reappeared: the spectrum of *trans*-2,3-epoxybutan-1-ol (III) has a band at 3583 cm^{-1}, as is shown in Fig. 1 and Table 1.

These results may be interpreted as follows. In order to establish the intramolecular hydrogen bond between the hydroxyl group and the oxygen of the oxirane, the hydroxyl group must approach one of the lone-pair orbitals of the oxygen which are directed up and down in relation to the ring. However, if that conformation is taken in 2,3-epoxy-3-methylbutan-1-ol, the repulsive interaction between the *cis*-methyl and hydroxyl groups will be severe. Thus, the conformation is not favored in the case of compound II. Compound III, which lacks the *cis*-methyl group, has no severe interaction which would prevent the approach, and the O–H···O hydrogen bond is favored to show a band at 3583 cm^{-1}.

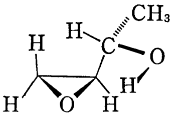
Although the band below 3600 cm^{-1} is lacking for compound II, a band is still observed at 3612.4 cm^{-1} which is attributable to the intramolecularly O–H··· oxirane interacting species. This fact offers support to the idea that the O–H···oxirane interaction takes place if the OH group approaches the ring within the plane of the ring, as was the case in O–H···cyclopropane interaction.[2] That is, edge-interaction is the favored process.

The absorption frequency (3590 cm^{-1}) of the intramolecularly O–H···O hydrogen-bonded species of glycidol (I) is higher by *ca.* 10 cm^{-1} than those of the glycidols (III, IV) which carry methyl groups. On the other hand, *trans*-2,3-epoxy-3-phenylpropan-1-ol (V), which is a phenyl-substituted glycidol, shows an absorption at almost the same frequency as glycidol itself. These results certainly reflect the electronic effect of the substituents.

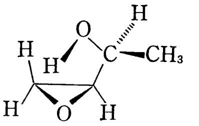
The absorption frequencies (*ca.* 3610 cm^{-1}) due to the intramolecularly O–H···oxirane interacting species of glycidol and its homologs are apparently lower than those of the O–H···cyclopropane species.[2] This means that the electron density at the site in the acceptor is higher than that of cyclopropane, because the conformational situations are quite analogous. It can, then, be suggested that the interacting electron orbitals are not of the C–C bond, but of the C–O bond of the ring, because it is the C–O bond, not the C–C, which has a higher electron density than the C–C bond of the cyclopropane.

As to the substituent effect, there is another interesting phenomenon in connection with 3,4-epoxybutan-2-ol (VI), which is believed to be of steric origin. That is, this compound shows no band due to the free OH group. Instead, two bands are observed at 3573 and 3607.0 cm^{-1}; the former can be attributed to the O–H···O bonded species, and the latter, to the O–H··· oxirane interacting species. To understand why this compound does not show any free OH, the conformational consideration is very helpful. Since this alcohol contains two asymmetric carbons, there are a pair of racemates. The method of preparation, *i.e.*, the epoxidation of 3-buten-2-ol with perbenzoic acid, suggests that the alcohol which is under investigation is the *threo* isomer, since it is known that the application of the same procedure to 4-methyl-3-penten-2-ol gives rise to a *threo* isomer of 3,4-epoxy-4-methylpentan-2-ol (VII), as will be discussed later. Therefore, there are three conformations (VIa, VIb, and VIc) to be considered with respect to the rotation about the C_2–C_{OH} bond.

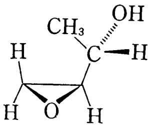
The H-inside conformation (VIa) has nothing unfavorable about it, because the repulsive interaction between hydrogens at C_3 and α to the hydroxyl group should be small. In addition, VIa can be stabilized because of the interaction between the hydroxyl group and the oxirane ring.



VIa



VIb



VIc

The OH-inside conformation (VIb) is unfavorable because of the steric interference between the hydrogen at C_3 and the OH group. However, this conformation can be stabilized due to the O–H···O bond formation.

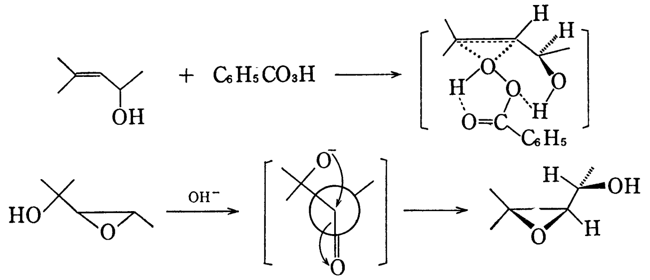
On the other hand, the CH_3-inside conformation (VIc) is unfavorable because of the repulsion between the hydrogen at C_3 or the lone pair of the oxygen atom of the ring and the methyl group, and there is nothing to favor the conformation; it could be considered that the intramolecular interaction between the hydroxyl group and the electrons of the C–C bond in oxirane can take place, but this interaction would be of a very weak nature, if it existed at all, judging from a theoretical consideration of the electron density and the experimental evidence which will be given later.

Thus, the population of the VIc conformation must be small and O–H-free conformations within the skeletal frames of VIa and VIb must also be scarce, thus reducing the intensity of the free O–H band.

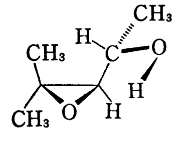
These results, together with the theoretical background, forced us to search for possible experimental evidence which clearly shows that the electron density at the C–C bond of the oxirane ring is really low. Thus, another approach has been undertaken: compounds which involve more severe steric requirements have been sythesized and their spectra examined.

The *threo* and the *erythro* isomers of 3,4-epoxy-4-methylpentan-2-ol (VII and VIII) have been selected as examples to study because the methyl group at C_3 exerts a severe steric effect and any conformational preference will thus be sharper than with compound

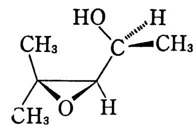
VI. The *threo* isomer (VII) has been obtained by the epoxidation of 4-methyl-3-penten-2-ol with perbenzoic acid. A consideration of the transition state of the epoxidation leads to the conclusion that the *threo* isomer is the main product, since it is a well-known fact that the peroxy acids attack the olefinic bond from the *cis* side of the hydroxyl group, probably because of the stabilization due to hydrogen-bond formation. This tentative conclusion is supported by the identity of the physical properties of the isolated product with those of the known *threo* isomer, which can be prepared by the isomerization of *cis*-3,4-epoxy-2-methylpentan-2-ol with the base.[7] The *erythro* isomer has been prepared by the isomerization of *trans*-3,4-epoxy-2-methylpentan-2-ol with the base.[7]



In the *threo* isomer VII, the H-inside conformation (VIIa) is the most stable, because the steric repulsion between the $CH_3CH(OH)$ group and the methyl group at C_3, which is *cis* to the $CH_3CH(OH)$ group, is the least. In addition, this conformation favors the intramolecular O–H···oxirane interaction. On the other hand, the O–H inside conformation (VIIb), which has the OH group above the ring, suffers from a severe steric interaction between the OH group and the methyl group at C_3, although this conformation may be stabilized due to the formation of the O–H···O bond. Thus, it can be concluded that the VIIb conformation is less stable than the VIIa conformation. The CH_3-inside conformation may be disregarded because its inner strain is high.



VIIa



VIIb

The absence of any absorption below 3600 cm^{-1} and the presence of two ν_{O-H} bands at 3607.4 and 3628 cm^{-1} (Fig. 2 and Table 1) for Compound VII support the above discussion. The absorption at the higher frequency, which is assigned to the free OH group, is weak, and the band at the lower frequency is strong, also suggesting that the O–H···oxirane interaction is an exothermic process to a considerable extent.

In the *erythro* isomer VIII, if the hydroxyl group is to interact with the C–O of the oxirane ring, the methyl-inside conformation (VIIIa) must be taken. This conformation is, however, apparently unfavorable because of the severe interaction between the methyl group at C_3 and the $CH_3CH(OH)$ group. On the other hand, such a repulsive interaction will be less when H-inside conformation (VIIIb) is taken. In the VIIIb conformation, the O–H group may approach the C–C bond of the oxirane ring, but it is impossible for it to approach the C–O of the ring.

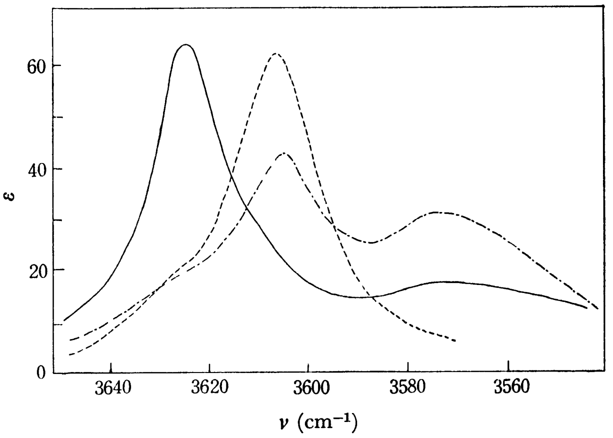
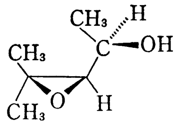
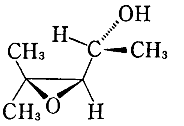


Fig. 2. ν_{O-H} absorption bands of *threo* (VII; ------) and *erythro* (VIII; ——) isomers of 3,4-epoxy-4-methylpentan-2-ol, and *trans*-3,4-epoxypentan-2-ol (IX; —·—).



VIIIa



VIIIb

In reality, the ν_{O-H} spectrum of VIII shows absorptions at 3623.6 and 3567 cm^{-1}, the former being by far the strongest band. Besides, the presence of a weak band at 3612 cm^{-1} is suggested by the separation of the observed band into symmetrical component bands. The results indicate that the intramolecular interaction between the OH group and the orbitals involved in the C–C bond is a very weak one, if there is any at all. If the C–C bond is really interacting, then Compound VIII should also have shown a strong band attributable to the O–H···oxirane interaction.

The discussions of the stable conformations of the diastereomers given above are also supported by the NMR spectra. The vicinal coupling constants (J_{vic}) of the ring proton with the α-protons of the *threo* and *erythro* isomers were 8.0 and 8.5 Hz respectively. The larger values of J_{vic} suggest that the average torsional angles made by the two H–C_{methine} bonds are large;[10] that is, the populations of the H-inside conformers, VIIa and VIIIb, are large.

The steric effects of the *cis*-methyl group are clear from the spectrum of the *threo* isomer of *trans*-3,4-epoxypentan-2-ol (IX), which corresponds to a compound in which the *cis*-methyl group of the *threo*-3,4-epoxy-4-methylpentan-2-ol (VII) has been removed. IX shows a strong O–H···O-bonded band (Fig. 2), in contrast to the absence of the O–H···O bond in VII.

In view of the above discussions, it seemed that it would be interesting to examine the case where there were no small groups at the α-position of the alcoholic hydroxyl group. Thus, the ν_{OH} spectrum of 3,4-epoxy-

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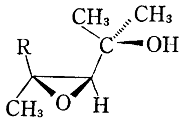
[10] K. Tori, T. Kameno, and T. Nakagawa, *J. Org. Chem.*, **29**, 1136 (1964).

2,4-dimethylpentan-2-ol (X) was measured; it gave absorptions at 3617 and 3559.4 cm^{-1}. Apparently the band at the higher frequency can be assigned to the free hydroxyl group,[9] and that at the lower frequency, to the O–H···O bonded form. On the other hand, *trans*-3,4-epoxy-2-methylpentan-2-ol (XI), which lacks the methyl group *cis* to the $C(CH_3)_2OH$, showed absorptions at 3598 and 3566.4 cm^{-1}. Thus, compound X can be regarded as existing as both free and O–H···O interacting species, whereas compound XI exists as both the O–H···oxirane-interacting and the O–H···O-bonded species.

In addition to the fact that the OH-inside conformation of compounds X and XI can be stabilized by forming an O–H···O hydrogen bond, the CH_3-inside conformation (Xa and XIa) is the least stable, because the van der Waals radius of oxygen is smaller than that of the methyl. Thus, in both cases, the O–H···O bonded species exist as the major components.

The cause of the presence of the O–H···oxirane interacting species in XI may be the relative bulkiness of the methyl group and hydrogen. Although the methyl-inside conformations (Xa and XIa) are more unstable than the OH-inside, such a confomration is not prohibitive if R is a hydrogen. If such a conformation is present, the O–H···oxirane interaction can be expected to occur to some extent. The Xa conformation is, however, almost prohibited because of the severe steric repulsion between the two methyl groups.



X_a: $R=CH_3$
XI_a: $R=H$

All the results presented above are explainable if the following two points are assumed: 1) the O–H···oxirane ring interaction takes place between the hydroxyl group and the C–O bond of the oxirane, but the interaction involving the C–C bond of the oxirane is negligible, and 2) the interaction takes place when the OH group approaches the oxirane ring within the plane of the ring.