The precision of the chromatographic separation alone was investigated by performing duplicate analyses on aliquots of impure solutions of codeine salts. The results of these analyses are shown in Table IV.

**Purity of the Codeine.** In the analysis of relatively pure samples the codeine eluted from the column is colorless and crystalline, but with very impure mixtures such as opium, the eluted codeine will vary from nearly colorless to light brown.

Figure 5 is a graph of the weights of a series of fractions obtained in the analysis of a sample of opium plotted as a function of fraction number. After being weighed the eluted alkaloid fractions were dissolved in 95% ethyl alcohol and the absorbances of the resulting solutions were measured at wave lengths of 275 and 290 mμ using a Beckman Model DU spectrophotometer. The ratio of the absorbance at 275 to that at 290 mμ was computed for each fraction and these ratios are also plotted in Figure 5. The same ratio was determined for pure codeine, thebaine, neopine, and papaverine and these values are shown in Table V.

**Table V. Absorbance Ratios for Pure Alkaloids**

| Alkaloid | Absorbance, 275/290 mμ |
|---|---|
| Codeine | 0.897 ± 0.005 |
| Thebaine | 0.859 ± 0.005 |
| Neopine | 1.29 ± 0.05 |
| Papaverine | 1.34 ± 0.05 |

The ratios for the fractions in the codeine peak are very close to that of codeine, and different from those of the probable impurities, indicating that the material is substantially pure codeine.

The melting point of the codeine in fraction 25 was 153.3° to 154.5° C., that of fraction 26 was 153.3° to 154.5° C., and that of fraction 27 was 149.4° to 151.0° C. The melting point of a sample of codeine of National Formulary IX quality was 155.4° to 156.2° C. These data further confirm the purity and identity of the material eluted from the column.

## ACKNOWLEDGMENT

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# Infrared Absorption Bands Characteristic of the Oxirane Ring

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**Part of the research program of this laboratory required the syntheses of a number of epoxy compounds. In a follow-up of this program there was need for suitable methods for detecting these different compounds. Infrared spectroscopy appeared to offer the best hopes of success. This involved a study of the infrared absorption spectra of the compounds. The infrared absorption of 26 epoxy compounds were recorded from 2 to 15 microns, in the liquid state and in solution. The presence of a characteristic absorption band at about 8 microns was confirmed and evidence compiled for two other characteristic absorption bands at about 11 and 12 microns. The position of the latter bands varied with the compound, ranging from 10.52 (950 cm.$^{-1}$) to 11.58 microns (863 cm.$^{-1}$) in the 11.0-micron position and from 11.57 (864 cm.$^{-1}$) to 12.72 microns (786 cm.$^{-1}$) in the 12-micron position. Some correlation between the wave-length position of the bands and the reactivity of the compounds with acetic acid was noted. This work adds to the knowledge of the infrared absorption spectra of epoxy compounds. It also establishes the existence of characteristic infrared absorption bands for the epoxide ring in the 10- to 13-micron region. Heretofore, evidence of this had been limited. The correlation between the wave-length positions of the bands and the reactivities with acetic acid is of considerable theoretical interest and of possible practical use.**

As POINTED out by Shreve, Heether, Knight, and Swern *(8)*, little has been reported on the infrared spectra of heterocyclic oxygen compounds. They added materially, however, to the published data by reporting on the infrared absorption spectra of 13 oxirane compounds plus tetrahydropyran, tetrahydrofuran, and dioxane. Previous to this, Barnes, Gore, Liddel, and Williams *(2)* had given a few spectra covering a limited range, and Field, Cole, and Woodford *(3)* had reported data on eight oxirane compounds.

The lack of spectral data is reflected in the fact that little is known about absorption bands which are characteristic of the epoxide ring (oxirane group). Herzberg *(5)*, using the results of Linnett, has discussed the infrared and Raman spectra of ethylene oxide and found that there are three wave lengths attributable to the oxygen ring—at 7.92, 11.56, and 12.38 microns (1262, 865, and 808 cm.$^{-1}$). Lespieau and Gredy *(6)* and Ballaus and Wagner *(1)* studied the Raman spectra of a number of simple epoxy compounds and found that the Raman shift at 1262 cm.$^{-1}$ (corresponding to infrared absorption at 7.92 microns) was constant, while the spectra in the 700- to 900-cm.$^{-1}$ region (13 to 11 microns) were so complicated that it was not possible to assign any frequency with certainty. Field, Cole, and Woodford *(3)* using the infrared apparently found similar conditions, as they concluded that only the 8-micron (1250-cm.$^{-1}$) band could be identified with reasonable certainty. Robinson in 1948 in this laboratory recorded the spectral region at about 8 microns for 19 oxirane compounds and showed that there was a strong ab-

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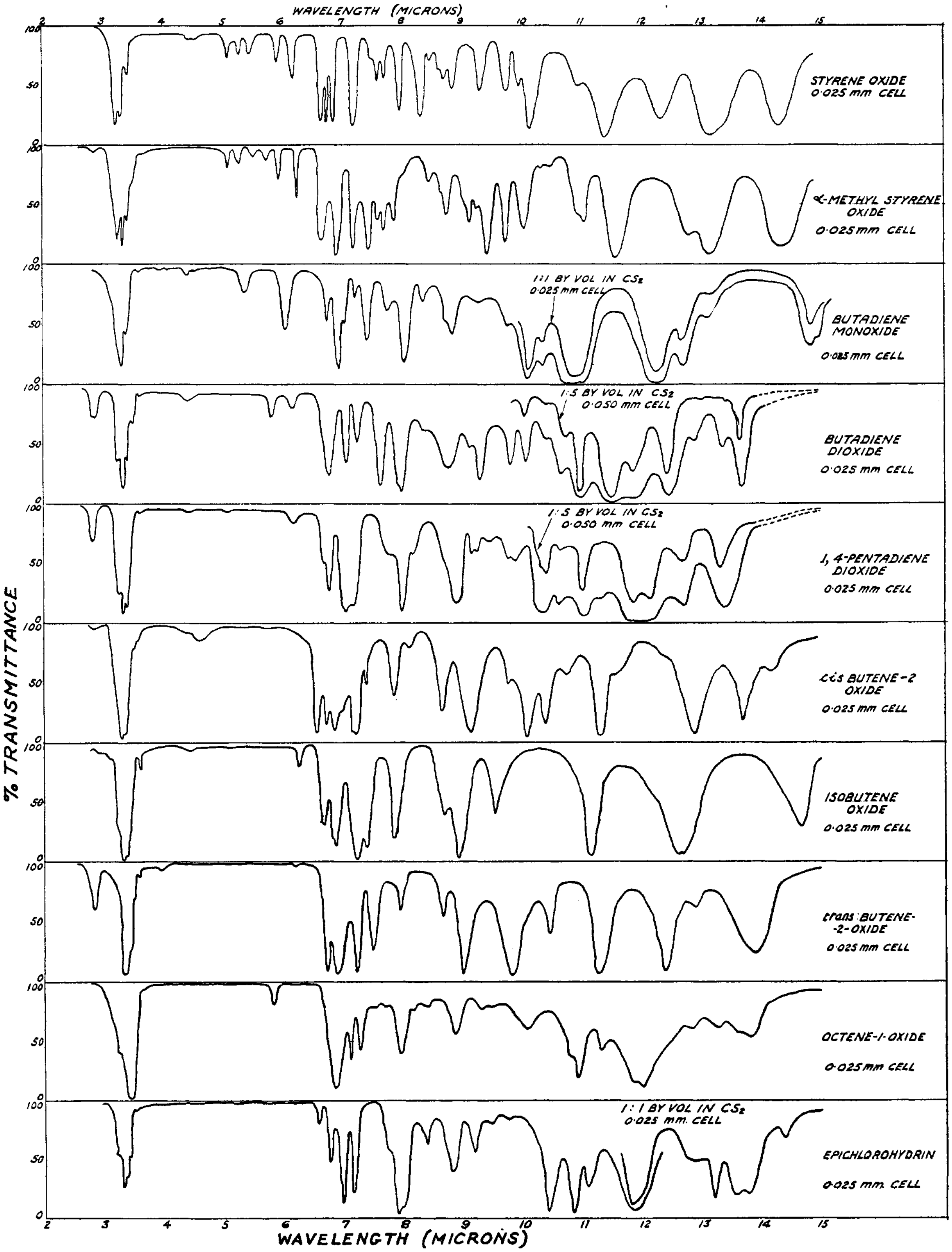

Figure 1. Epoxy Compounds of Hydrocarbons

sorption band which varied in position from 7.82 to 8.04 microns (1279 to 1244 cm.$^{-1}$), depending on the compound. The variation in band position with the compound is shown in Table I. The presence of a characteristic band at about this wave length is therefore fairly conclusive. Reference to the 26 spectra given here shows that the band is usually of good intensity and can be readily detected. A possible exception is α-methylstyrene oxide, the spectrum of which is discussed later in the paper.

**Table I. Epoxide Bands at about 8 Microns**

(D. Z. Robinson)

| Compound | Wave Length, Microns | Wave Number, Cm.$^{-1}$ |
|---|---|---|
| Phenoxypropylene oxide | 7.82 | 1279 |
| Butene-2-oxide | 7.84 | 1276 |
| Cyclohexadiene dioxide | 7.87 | 1271 |
| Epichlorohydrin | 7.88 | 1269 |
| Propene oxide | 7.90 | 1266 |
| Cyclohexene oxide | 7.92 | 1263 |
| Ethylcyclohexene oxide | 7.92 | 1263 |
| Vinylcyclohexene monoxide | 7.92 | 1263 |
| Glycidyl-2-tetrahydropyranyl ether | 7.93 | 1261 |
| Vinylcyclohexene dioxide | 7.95 | 1258 |
| Glycidyl methacrylate | 7.95 | 1258 |
| Vinylcyclohexane oxide | 7.96 | 1256 |
| Butadiene dioxide | 7.97 | 1255 |
| Styrene oxide | 7.97 | 1255 |
| Butyl glycidyl ether | 7.97 | 1255 |
| Diallyl ether dioxide | 7.97 | 1255 |
| Methoxy methoxy ethyl glycidyl ether | 7.97 | 1255 |
| Diallyl ether monoxide | 7.98 | 1253 |
| Butadiene monoxide | 8.04 | 1244 |

The first and only published success in detecting possible characteristic bands in the 11- to 13-micron region is that of Shreve, Heether, Knight, and Swern (*8*). They showed that oxirane derivatives of terminally monounsaturated compounds have two characteristic bands near 11 and 12 microns and that oxirane derivatives of cis monounsaturated fatty acids, esters and alcohols have a characteristic band at 11.8 to 12 microns, while those of the trans isomers have a band at 11.2 to 11.4 microns. They also showed that the spectra are dependent on the physical state of the compounds.

The present paper gives the infrared absorption spectra of 26 oxirane compounds from 2 to 15 microns and carries further the investigation of characteristic absorption bands in the 10- to 13-micron region of the spectrum.

## EXPERIMENTAL

**Instrumental.** The infrared spectrometer used was a Perkin-Elmer Model 12C. The gain was set for full scale recorder response with an applied voltage of 1.0 microvolt. The order of slit widths and speed changes are as follows:

| Spectral Range, Microns | Slit Width, Mm. | Speed |
|---|---|---|
| 1.9 to 3.75 | 0.019 | 4 |
| 3.75 to 5.45 | 0.031 | 4 |
| 5.45 to 7.45 | 0.058 | 2 |
| 7.45 to 8.9 | 0.105 | 2 |
| 8.9 to 11.6 | 0.150 | 2 |
| 11.6 to 13.4 | 0.250 | 1 |
| 13.4 to 15.0 | 0.400 | 1 |

The paper speed of the recorder is one half the normal rate, giving a spectral record size one half that which would normally be obtained at the indicated scanning speeds. This is a routine procedure in this laboratory and provides a more conveniently sized spectrum with little or no decrease in resolution. In the calculation of the values of the per cent transmittance, the readings of the spectrum of a blank cell in the case of pure liquids and of the solvent and cell in the case of solutions were subtracted from the corresponding readings obtained with the compound concerned. Pure liquids were run in a 0.025-mm. cell and solutions in 0.025-, 0.050-, or 0.100-mm. cells, depending on the concentration required.

The concentrations and cell thicknesses for solutions were chosen on the basis of the spectral curve for the pure compound in the 0.025-mm. cell and the relative solubility in the solvent. Where the dilution is low the concentration is expressed as a volume-volume ratio; where it is high it is expressed as percentage of solution. These cumbersome variations became necessary when it was found that the initial dilution procedure could not be followed for all compounds. The only solid, cyclohexadiene dioxide, was run in both carbon disulfide and carbon tetrachloride. Propylene oxide, a highly volatile liquid at room temperatures, was run in carbon disulfide.

**Materials.** Twenty-eight oxirane compounds were available for this work. The spectral range of 2 to 15 microns for 26 are given here. Only the 10- 15-micron range of the other two compounds, glycidyl linoleate and propylene oxide, were recorded. The purity of the linoleic acid used in the preparation of the former was unknown and the spectrum of the latter has been given by Shreve *et al.* (*8*). However, the long wave-length range of both compounds is used later to indicate the probability of characteristic bands. The spectra of two of the other compounds, styrene oxide and butadiene monoxide, have also been given by Shreve *et al.* They are included here to indicate the degree of correlation with their work.

With the exception of propene oxide, all of the epoxy compounds had been synthesized in this laboratory in the course of other research work. While they had been purified at the time of preparation, this had been done a year or two previous to the recording of the infrared spectra. They had, however, been kept under refrigerated conditions to prevent polymerization and isomerization. Further purification at this time might have been desirable, but the particular needs of this work did not warrant it. The majority of the oxides had been prepared from the unsaturated parent compounds; thus any impurity would probably be from this source. The ester epoxides, however, were prepared by reaction between epichlorohydrin and the potassium salt of the parent acid. Some of the spectra show bands in the bonded hydroxyl position, indicating some impurity from decomposition of the oxides. Oxide values were redetermined and are given in Table II. They are expressed as percentage of oxidation—i.e., a 100% oxidation would mean that all of the carbon-carbon double bonds at the particular location in the molecule had been oxidized to the epoxide. The values are not a good indication of purity, as the analytical method shows relatively wide variations from compound to compound and, in general, results can be as much as 5% low, as indicated by determinations on pure ethylene oxide.

The majority of the oxide determinations were made by a dioxane-hydrochloric acid method which is a modification of the usual ether-hydrochloric acid method. Several of the determina-

**Table II. Oxide Values of Oxirane Compounds**

| Compound | Theoretical Oxide, % | |
|---|---|---|
| | Dioxane–HCl | Pyridine–HCl |
| Styrene oxide | 75 | 96 |
| α-Methylstyrene oxide | 22 | 43 |
| Butadiene monoxide | 93 | ... |
| Butadiene dioxide | 90 | ... |
| 1,4-Pentadiene dioxide | 94 | ... |
| *cis*-Butene-2-oxide | 87 | ... |
| *trans*-Butene-2-oxide | 93 | ... |
| Isobutene oxide | 83 | ... |
| Octene-1-oxide | 96 | ... |
| Epichlorohydrin | 97 | ... |
| Glycidyl sorbate | 91 | ... |
| Glycidyl crotonate | 96 | ... |
| Glycidyl methacrylate | 95 | ... |
| Glycidyl butyrate | 98 | ... |
| Glycidyl linoleate | 92 | ... |
| Phenyl glycidyl ether | 98 | 100.7 |
| Diallyl ether monoxide | 94 | ... |
| Butyl glycidyl ether | 97 | ... |
| Methoxy methoxy ethyl glycidyl ether | No data | ... |
| *o*-Allyl phenyl glycidyl ether | 98 | ... |
| Diallyl ether dioxide | 90 | ... |
| 1,4-Butanediol diallyl ether dioxide | 99 | ... |
| Cyclohexene oxide | 98 | ... |
| 4-Vinylcyclohexene oxide[a] | 97 | ... |
| 4-Vinylcyclohexene dioxide | 91 | 96 |
| Vinylcyclohexane oxide | 83 | ... |
| Cyclohexadiene dioxide (high m.p. isomer 106.5° to 107.5° C.) | No data | ... |

[a] (4-Vinyl-1,2-epoxycyclohexane).

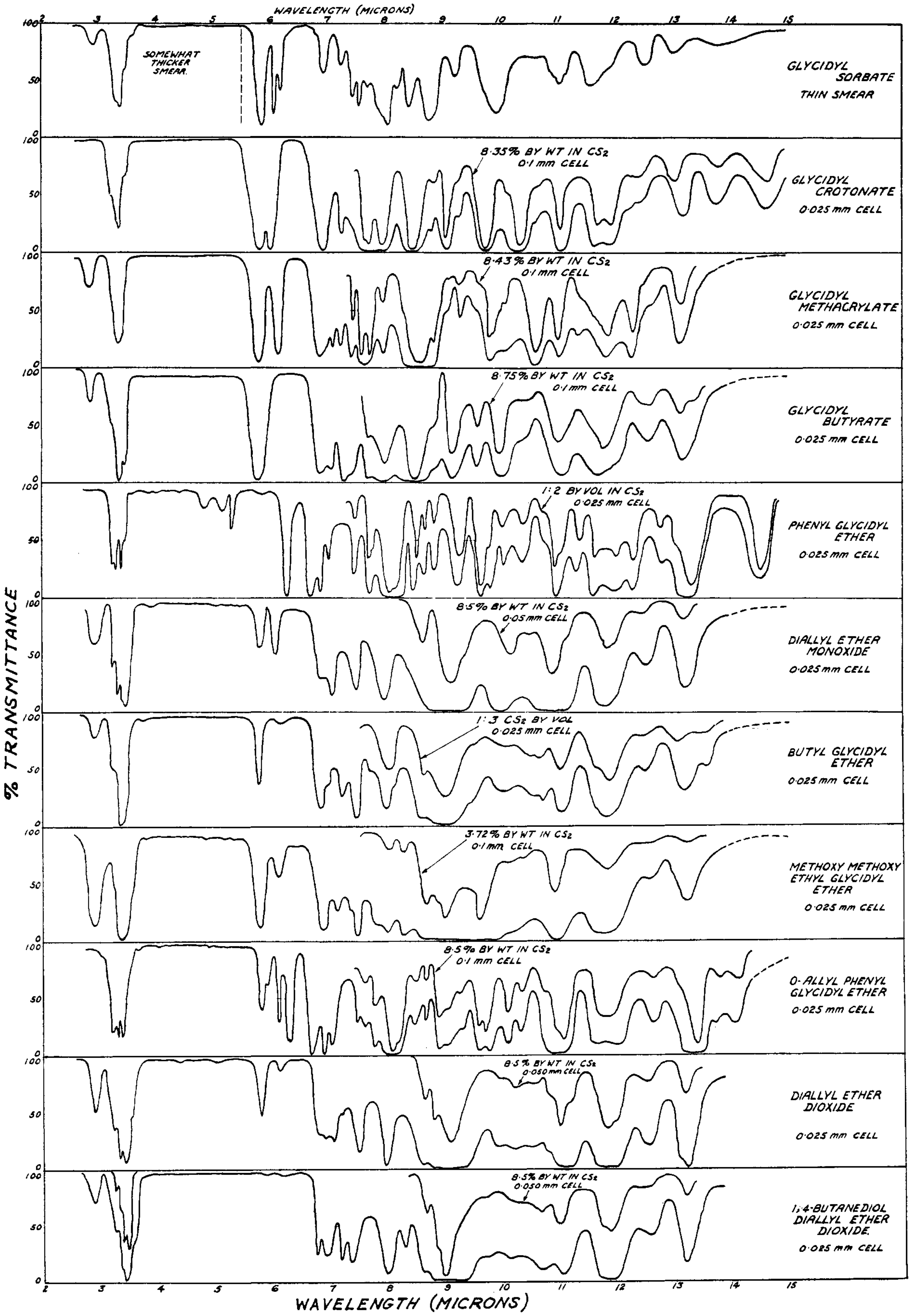

Figure 2. Epoxy Compounds of Esters and Ethers

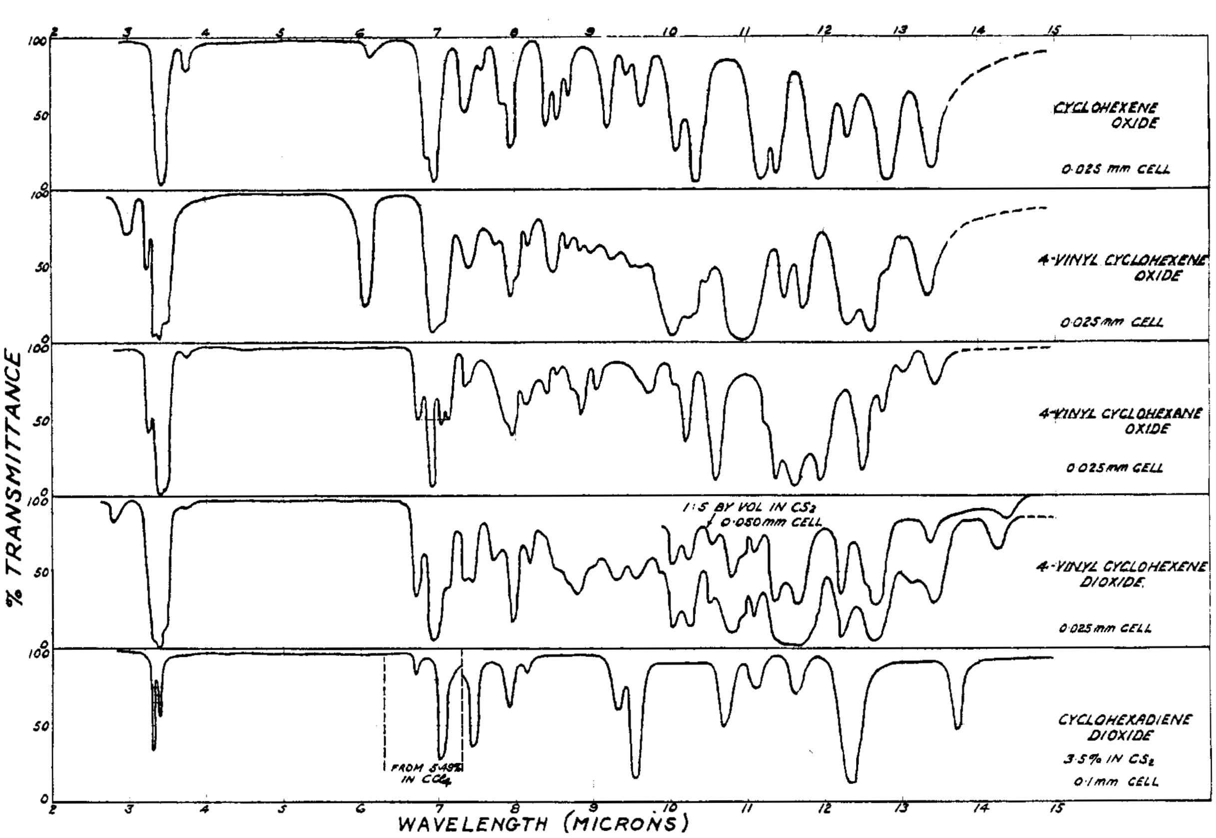

Figure 3. Cyclic Epoxides

tions were made with a pyridine-hydrochloric acid method, which appears to be more accurate in some cases. For example, it shows greatly increased oxide content for styrene oxide and $\alpha$-methyl styrene oxide. The low values for styrene oxide will be discussed later.

It is apparent that there is some uncertainty as to the purity of the compounds. The present purpose, however, was to investigate the 10- to 13-micron region for characteristic bands. As these should be fairly intense, the presence of a certain amount of impurity should not cause marked interference with this purpose. On the other hand, the spectra would probably be of interest to others and are given here with the previous cautionary remarks. A comparison of the spectra of styrene oxide and butadiene monoxide with those recorded by Shreve *et al.* (*8*) shows little or no difference, and this may be taken as a good indication of the reliability of the majority of the spectra.

## DISCUSSION OF RESULTS

**General Comments and 8-Micron Band** (1250 Cm.$^{-1}$). The spectra in the 2- to 15-micron region are given in Figures 1 to 3. The ten oxides in Figure 1 are derived from unsaturated hydrocarbons and include two dioxides. In Figure 2 are four epoxy esters and seven epoxy ethers; two of these compounds are dioxides. Four of the oxides of Figure 3 are derived from unsaturated cyclic compounds and include two dioxides. Vinylcyclohexane oxide is included in this figure. No significant attempt has been made to determine if all the bands of a given spectrum are due to the epoxy compound; however, 13 of the spectra have a band of varying intensity at 2.8 microns, indicating some decomposition of the epoxide ring. A moderately intense band at 5.8 microns in five of the ethers does not appear consistent with these compounds. However, the assignment to a configuration derivable from them in the parent compounds is not apparent, unless it is an aldehyde or ketone. The band at about 8 microns attributed to the epoxide ring is readily detectable in all the spectra with the exception of $\alpha$-methylstyrene oxide. In the latter case it is questionable if the band exists. The spectrum from 7.8 to 8.5 microns (1282 to 1176 cm.$^{-1}$) is curiously similar to that of $\alpha$-methylstyrene, the parent compound of this oxide. This might be attributed to the low oxide value, 43%, and could indicate that most of the sample was still $\alpha$-methylstyrene. This is not borne out by the intensity of the C=C vibration at 6.25 microns (1600 cm.$^{-1}$) nor the vinyl vibration at 11.2 microns (893 cm.$^{-1}$). In fact, the band that might be attributed to the latter vibration appears to have shifted to about 11.05 microns (905 cm.$^{-1}$). As will be shown later the very intense band at 11.58 microns (864 cm.$^{-1}$) can be attributed to the epoxide ring and this would indicate high oxide content, at least similar to that of the styrene oxide, where the analogous band is at 11.4 microns (877 cm.$^{-1}$). This supports the belief of the chemists who synthesized the compound that the 43% oxide value is far from the true value. Part of the reason for this is that a higher value was obtained for the oxide content with a better method of analysis. It is believed that rearrangement takes place in this molecule on the addition of the acid in the first part of the oxide determination and an even better method of analysis would give a higher oxide value. [Lord (*7*) has suggested that the 11.05-micron (905 cm.$^{-1}$) band is due to the presence of unreacted styrene. He has indicated that the intensity of this band could thereby account for a large amount of the missing oxide value. This implies either a decomposition of the $\alpha$-methylstyrene during the epoxide reaction or the presence of styrene in the original $\alpha$-methylstyrene. The author has not had time to resolve this point, but offers it as a possible alternate explanation.] On this basis it would seem that there is no band at about 8 microns for $\alpha$-methylstyrene oxide with characteristics similar to those of the 8-micron bands in the spectra of the other oxides. It is apparent that further investigation is needed to resolve this point.

**Epoxide Bands in 10- 13-Micron Region.** The search for characteristic epoxide bands in the 10- 13-micron region was done by comparing the epoxy spectra with those of the saturated and in some cases the unsaturated derivatives. This is essentially the same procedure as that of Shreve *et al.* (*8*). Their problem was somewhat simpler, in that any marked changes in the spectra of the long-chain fatty acids, esters, and alcohols could be reliably associated with the additions of the epoxide ring. The majority of the compounds used in the present work are relatively small and it was highly probable that the spectra would be changed considerably. However, general observation of the spectra of the epoxy compounds derived from hydrocarbons showed that in the 10- 13-micron region the bands are considerably more intense than those of the hydrocarbon, the relative intensity depending on the size of the hydrocarbon molecule and the number of carbon-carbon double bonds also present. It might thus be assumed that strong bands appearing in the region are connected with vibrations of the oxide ring unless they can be otherwise allocated. This was a primary consideration in picking out the bands. For convenience the 10- 15-micron parts of the spectra are repeated along with the spectra of related hydrocarbons in Figures 4 to 16.

**Styrene Oxide and α-Methylstyrene Oxide.** In Figure 4 the spectra of styrene oxide, α-methylstyrene oxide, styrene, α-methylstyrene, ethylbenzene, and isopropylbenzene are shown. It is apparent that the most marked differences between the spectra of the benzene compounds and the oxides are the bands marked by triangles at 11.40 (877 cm.$^{-1}$) and 12.31 microns (812 cm.$^{-1}$) in styrene oxide and 11.58 (863 cm.$^{-1}$) and 12.72 microns (786 cm.$^{-1}$) in α-methylstyrene oxide. The choice of these as the oxide vibrations implies that the bands are shifted to longer wave lengths with the addition of a methyl group at the α-carbon. Reference to the spectra of styrene and α-methylstyrene shows that this is consistent with a shift of the well-known vinyl vibration at 11.0 microns (909 cm.$^{-1}$) in styrene to 11.2 microns (893 cm.$^{-1}$) in α-methylstyrene, indicating that the α-methyl can shift the side-chain vibration in this manner. It is true that the 13.45 micron (743 cm.$^{-1}$) band in ethylbenzene is shifted to 13.2 microns (757 cm.$^{-1}$) in isopropylbenzene, but this strong band along with that at 14.2 microns (704 cm.$^{-1}$) appears in all six spectra and must be associated with the benzene ring. This also excludes the possibility that the chosen bands are connected with the benzene vibrations, leaving the oxide ring as the most probable allocation for bands of such intensity.

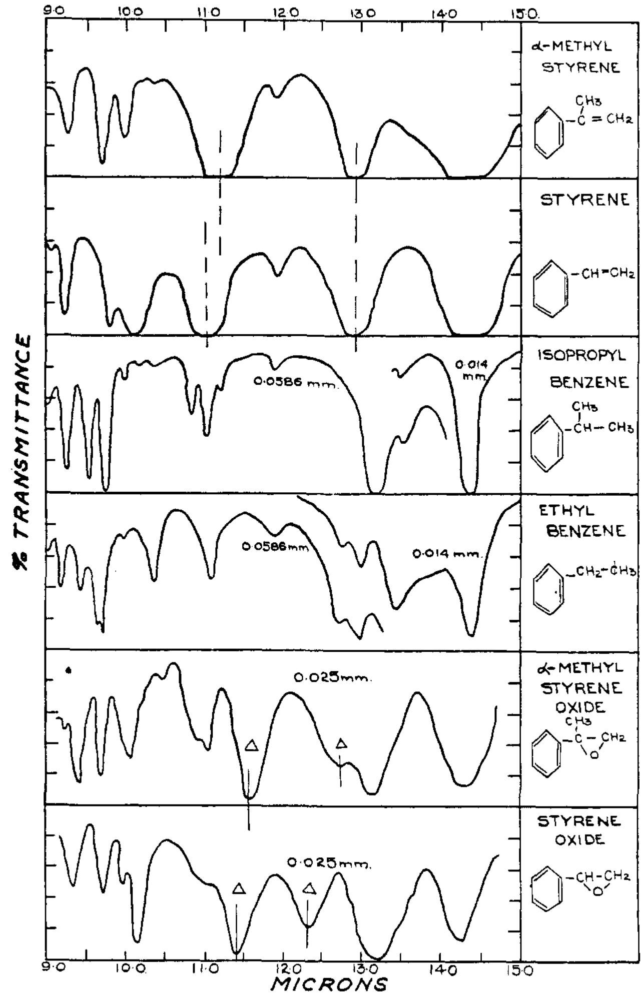

Figure 4. Spectra of Styrene Oxide and Methylstyrene Oxide

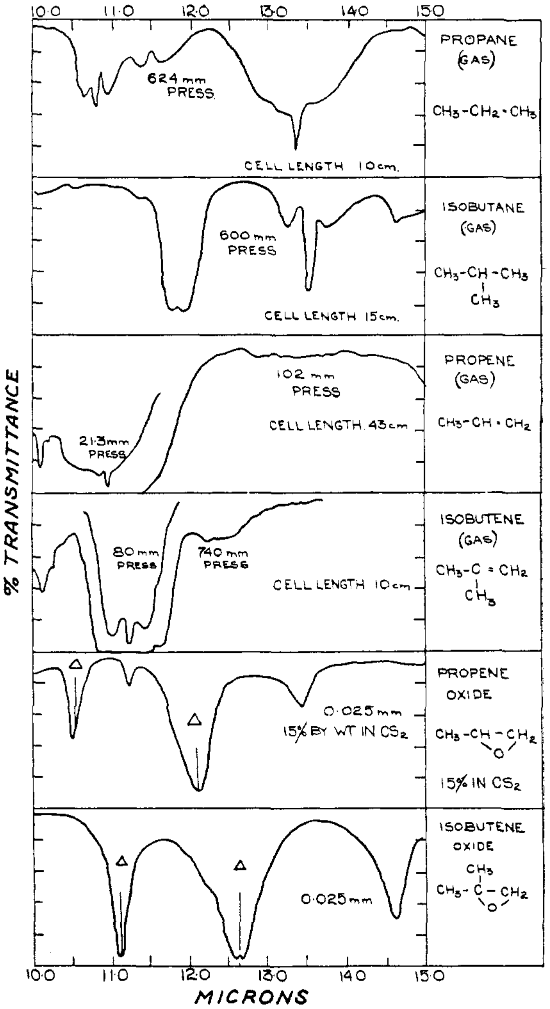

Figure 5. Spectra of Propene Oxide and Isobutene Oxide

**Propene Oxide and Isobutene Oxide.** Propene oxide and isobutene oxide, Figure 5, illustrate further the effect of α-methyl substitution. Here again there is the shift to a longer wave length of the vinyl vibration on the addition of the methyl group. There is a similar and even greater shift of a band in propane and isobutane. In the propene and isobutene spectra the bands attributable to the vinyl vibrations are much more intense than any of the bands in propane and isobutane. Strong bands appearing in this spectral region of the oxide are presumably due to the oxide ring, since the vinyl vibration would disappear. The bands chosen are 10.52 and 12.09 microns (950 and 827 cm.$^{-1}$) for propene oxide and 11.11 and 12.56 microns (900 and 796 cm.$^{-1}$, first of double band) for isobutene oxide, based upon the wavelength shift. Shreve *et al.* (*8*) give the spectrum of propene oxide in the pure liquid state and show a double band at 12.09 microns. Only a single band was detected in this work which might be due to the fact that it was in a solution of carbon disulfide. The shape of the band obtained by Shreve *et al.* is analogous to that at 12.56 microns for isobutene oxide in the pure liquid state and is a good indication that this is the band that has been shifted by the addition of the methyl group.

***cis*- and *trans*-Butene-2-Oxide.** The spectra of *cis*- and *trans*-butene-2-oxide, along with the saturated and unsaturated derivatives are given in Figure 6. The probable oxirane ring bands are 11.29 and 12.87 microns (886 and 777 cm.$^{-1}$) for *cis*-butene-2-oxide and 11.27 and 12.32 microns (887 and 812 cm.$^{-1}$) for *trans*-butene-2-oxide. A small band at 12.32 microns (812 cm.$^{-1}$) in *cis*-butene-2-oxide and another at 12.87 microns (777 cm.$^{-1}$) in *trans*-butene-2-oxide indicates the presence of the other isomer as an impurity in each oxide. The choice of these bands is based upon intensity considerations.

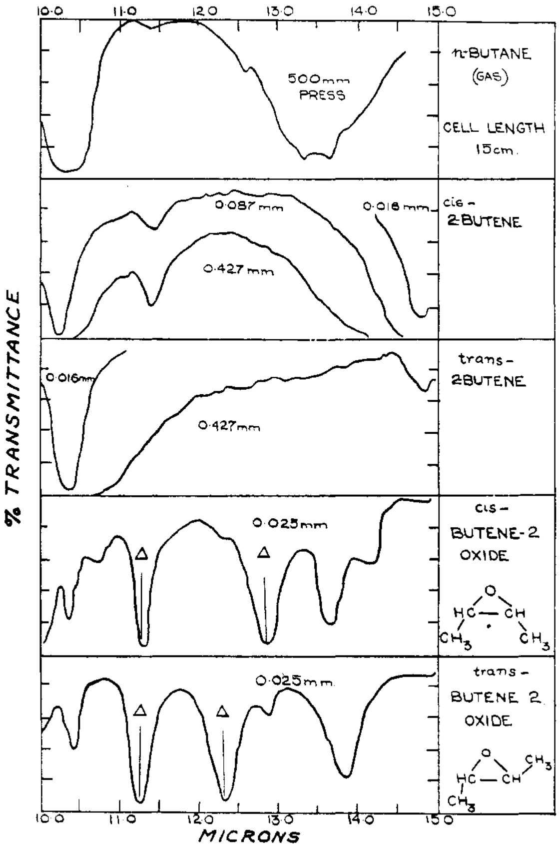

Figure 6. Spectra of Butene-2-oxide and Derivatives

**Octene-1-oxide and Epichlorohydrin.** Figure 7 shows the spectra of octene-1-oxide and epichlorohydrin with derivatives. The probable epoxide bands in octene-1-oxide are at 10.89 and 11.97 microns (918 and 835 cm.$^{-1}$). All other bands can be accounted for by similarities and intensity relationships with the derivatives. The 11-micron band in octene-1-oxide would disappear and the appearance of any strong band at about this wave length for the oxide would be associated with the epoxide ring. The bands chosen are in agreement with the results of Shreve *et al.* on decene-1-oxide, dodecene-1-oxide, and tetradecene-1-oxide; these authors concluded by comparison with the spectra of *n*-decane that epoxide bands are present at 10.9 and 12.0 microns.

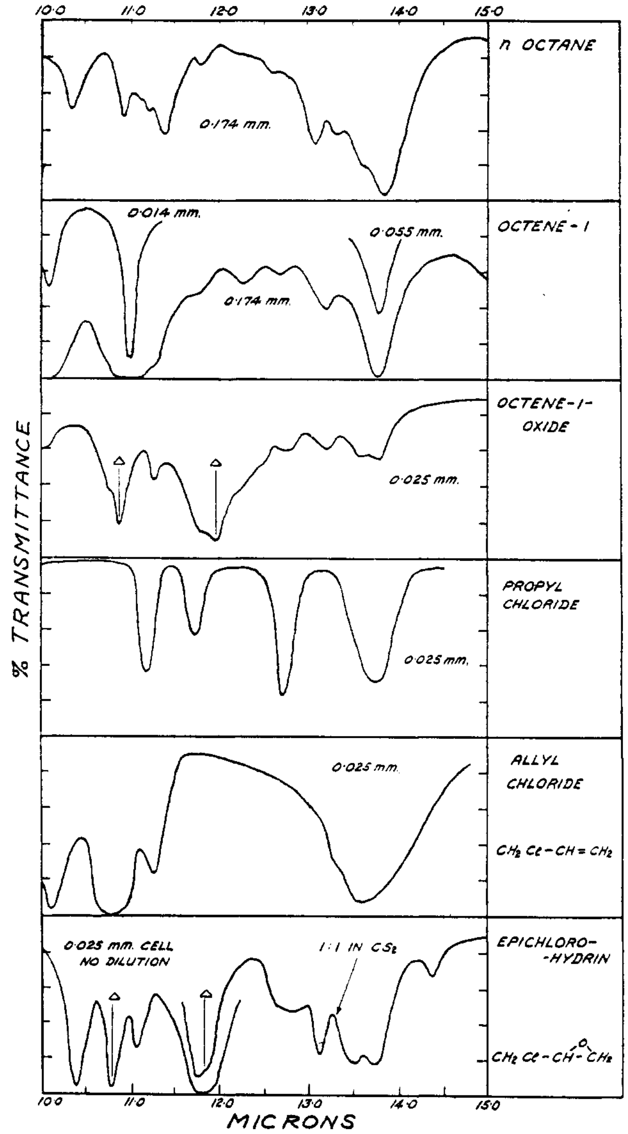

Figure 7. Spectra of Octene-1-oxide and Epichlorohydrin with Derivatives

The spectrum of epichlorohydrin offers a number of possible bands, that at 10.80 microns (926 cm.$^{-1}$) being a good possibility because of its intensity and the fact that it does not appear in propyl chloride; a band in the same position in allyl chloride is evidently due to the vinyl group and would disappear in the oxide. The band at 11.0 microns (909 cm.$^{-1}$) is rejected because of its low intensity and the fact that similar bands appear in both propyl chloride and allyl chloride. The band at 10.4 microns (962 cm.$^{-1}$) in the oxide could be associated with the 10.2-micron (980 cm.$^{-1}$) band in allyl chloride. The strong broad band at about 11.8 microns (847 cm.$^{-1}$) appears to be due to two bands, with the possibility that a band similar to the 11.7-micron (855 cm.$^{-1}$) band of propyl chloride interferes. The intensity favors an oxide band and the shape of the curve might be explained on the basis of an oxide band at 11.8 microns with interference from another band at 11.7 microns. The chosen bands are thus at 10.80 (926 cm.$^{-1}$) and 11.80 microns (847 cm.$^{-1}$).

**Butadiene Monoxide, Butadiene Dioxide, and 1,4-Pentadiene**

**Dioxide.** The spectra of these three oxides along with *n*-butane, 1-butene, and butadiene are shown in Figure 8. The strong band at 12.24 microns (817 cm.$^{-1}$) in butadiene monoxide is the best possibility for an epoxide vibration. The second epoxide band is very probably concealed in the broad band at 10.88 microns (919 cm.$^{-1}$) representing the vinyl group still left in this molecule. A glance at the spectrum of 1-butene shows that the same band in butadiene monoxide is much wider, indicating the probability that there are two bands here. Additional evidence for this is the presence of a band at 10.9 microns (917 cm.$^{-1}$) in the two dioxides when no vinyl groups are present.

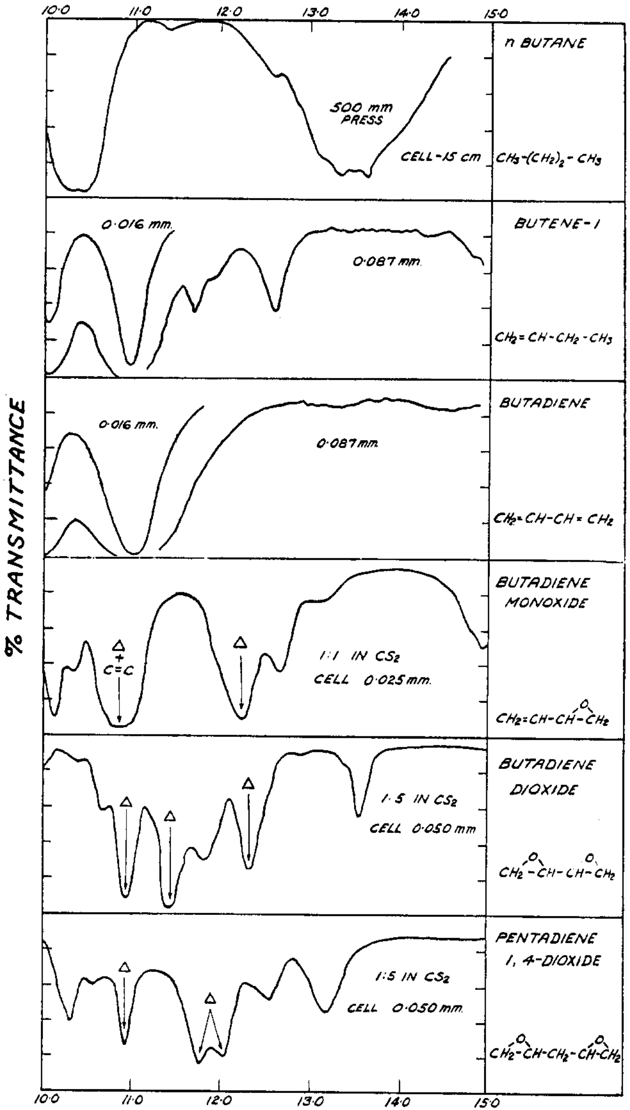

Figure 8. Spectra of Butadiene Monoxide, Butadiene Dioxide, and 1,4-Pentadiene Dioxide

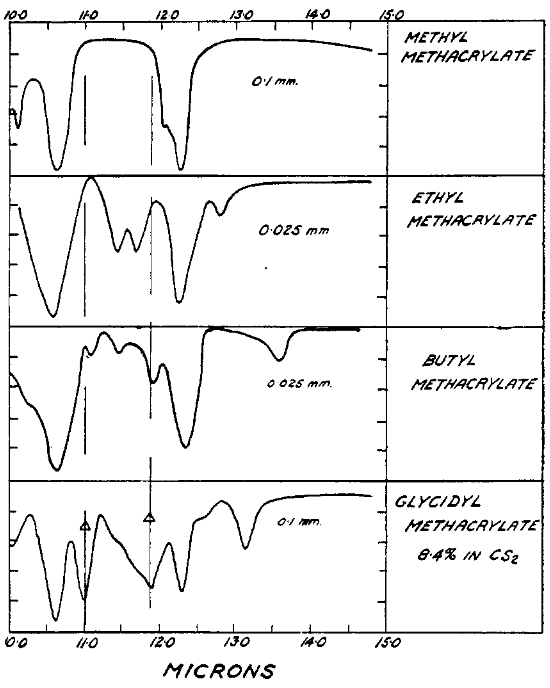

Figure 9. Spectra of Methacrylates

The spectra of the two dioxides shown are much more complicated and no definite conclusions have been drawn. In both there are three or four bands which could be due to epoxide vibrations based upon intensity considerations (note the dilution 1 to 5 by volume in carbon disulfide). The 10.9-micron (917 cm.$^{-1}$) band in both is probably an epoxide vibration in line with other epoxides. Butadiene dioxide has a band at 12.34 microns (810 cm.$^{-1}$) which would correspond to the 12.24-micron (817 cm.$^{-1}$) band in butadiene monoxide. However, the most intense band is at 11.48 microns (871 cm.$^{-1}$) and this must also be an oxide vibration. The band at 13.60 microns (735 cm.$^{-1}$) is also a strong band considering the dilution, but this is probably due to the chain. This might also be true of the 13.24-micron (755 cm.$^{-1}$) band in 1,4-pentadiene dioxide. The spectrum of 1,4-pentadiene dioxide differs from that of butadiene dioxide in that the strong band at 12.34 microns (810 cm.$^{-1}$) has disappeared and a band of much lesser intensity appears at 12.62 microns (792 cm.$^{-1}$); there are two strong bands at 11.80 (847 cm.$^{-1}$) and 12.06 microns (829 cm.$^{-1}$). A possible explanation of these two spectra is that in butadiene dioxide the two adjacent oxirane rings interfere with

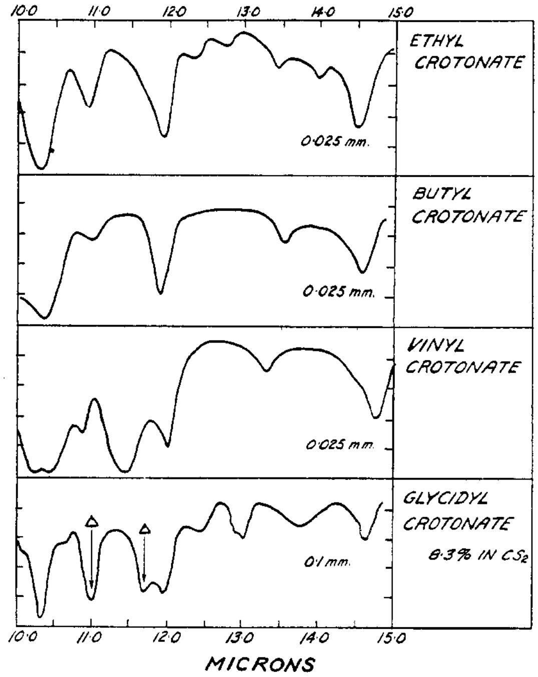

Figure 10. Spectra of Crotonates

each other, while in 1,4-pentadiene dioxide the intervening methylene group reduces the amount of interaction with the result that the spectrum will resemble more closely that of a single monoxide. The ultimate spectrum, except for increased intensity, resembles that of octene-1-oxide if more methylene groups were added. The latter has bands at 10.89 (918 cm.$^{-1}$) and 11.97 microns (835 cm.$^{-1}$).

**Epoxides in Esters.** All of the epoxy esters studied were of the glycidyl type. In two cases the presence of the oxirane bands was determined by comparing the spectrum of the epoxide with esters made from the same acid but with different alcohols. Figure 9 shows the spectral comparison of glycidyl methacrylate with methyl, ethyl, and butyl methacrylate. The propyl ester was not available. It is evident that there are two strong bands at 10.99 (910 cm.$^{-1}$) and 11.86 microns (843 cm.$^{-1}$) which are not present in the three other esters and thus could be attributed to the oxirane ring. In Figure 10, glycidyl crotonate is compared with ethyl, butyl, and vinyl crotonate, the propyl ester again not being available. The oxirane bands are at 11.03 and 11.68 microns (907 and 856 cm.$^{-1}$), the former because of its intensity. There is a similar band of much lesser intensity in the other esters and the 11.68-micron band is not present at all in the other esters. The band at 11.4 microns in vinyl crotonate is evidently due to the vinyl group.

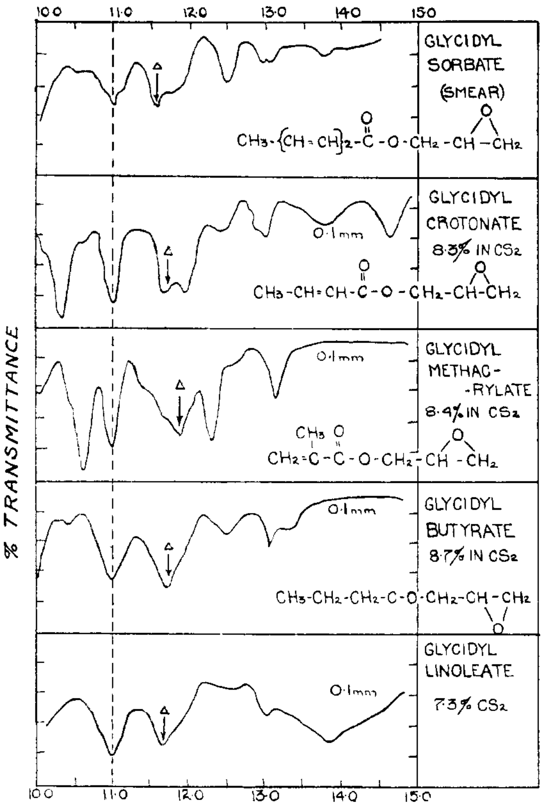

Figure 11. Spectra of Esters

Comparison spectra were not run for the three other esters—glycidyl sorbate, glycidyl butyrate, and glycidyl linoleate. Their spectra, however, are compared with those of glycidyl crotonate and glycidyl methacrylate in Figure 11. Strong bands appear at 11.0 microns and from 11.5 to 11.9 microns in all five esters and since those for glycidyl crotonate and glycidyl methacrylate have been attributed to the oxirane ring, it is reasonable to suppose the bands in the other esters are also from the oxirane ring. Certainly strong characteristic bands for esters are not generally found in this region and, except for the oxirane ring, the ester configuration is the only one common to the five spectra which might cause strong bands with so little change in wavelength positions. The bands for glycidyl butyrate are at 10.98 (911 cm.$^{-1}$) and 11.71 microns (854 cm.$^{-1}$), those for glycidyl linoleate at 11.00 (909 cm.$^{-1}$) and 11.67 microns (857 cm.$^{-1}$), and those for glycidyl sorbate at 11.01 (908 cm.$^{-1}$) and 11.57 microns (864 cm.$^{-1}$). There is a possibility that the 11.88 microns (842 cm.$^{-1}$) band of glycidyl sorbate instead of the 11.57-micron band is that belonging to the oxide vibration, but the higher intensity along with the oxirane band in glycidyl crotonate being at about the same position favors the latter choice.

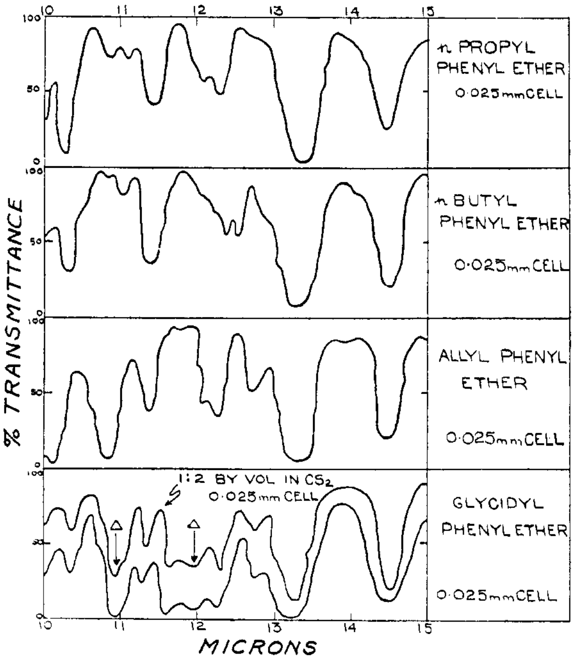

Figure 12. Spectra of Ethers

**Epoxy Ethers.** In Figures 12 and 13, three of the epoxy ethers are compared with similar hydrocarbon ethers. In Figure 12 glycidyl phenyl ether is compared with *n*-propyl phenyl ether, *n*-butyl phenyl ether, and allyl phenyl ether. The strong 10.8-micron (926 cm.$^{-1}$) band in allyl phenyl ether is evidently due to the vinyl group and would disappear in the oxide. Therefore, the strong band at 10.90 microns (917 cm.$^{-1}$) in glycidyl phenyl ether is probably due to the oxirane ring. The second epoxide band is probably at 11.95 microns (837 cm.$^{-1}$). There is a second band at about 11.0 microns (909 cm.$^{-1}$) which might be attributed to the epoxide, but its intensity is relatively low and it would be necessary to attribute the 10.90-micron band to some nonoxidization of the vinyl group. However, the oxide values for this compound are about 100%, eliminating this possibility. In Figure 13 butyl glycidyl ether and diallyl ether monoxide are compared with *n*-butyl ether, butyl ethyl ether, and allyl ethyl ether. Intensity values of the bands of the pure liquids for the same cell thickness indicate epoxide bands at 10.94 (914 cm.$^{-1}$) and 11.84 microns (844 cm.$^{-1}$) for butyl glycidyl ether and at 10.86 (921 cm.$^{-1}$) and 11.82 microns (846 cm.$^{-1}$) for diallyl ether monoxide. In the latter oxide there would be a band at 10.88 microns (919 cm.$^{-1}$) because the vinyl group is still present. However, the great increase in the intensity of the band at this point in the epoxide would indicate that the epoxide band is also present. The band at 11.0 microns in butyl glycidyl ether appears to be double with peaks at 10.94 (914 cm.$^{-1}$) and 11.03 microns (907 cm.$^{-1}$). There is a strong band at 13.2 microns in each oxide which is not present in the hydrocarbon ethers. The possibility that this is due to the oxirane ring cannot be ignored, although it is relatively much weaker than the other two bands. As shown in Figure 14, it is present in all seven of the epoxy ethers. A similar band occurs in all the esters at about the same wave length; it occurs also in 1,4-pentadiene dioxide and is barely visible in butadiene monoxide. It also appears in epichlorohydrin, propene oxide, and octene-1-oxide. However, strong bands also appear in this general position for *n*-butane, *n*-propane, and isobutane; weaker bands appear in some of the spectra of the other nonepoxy compounds.

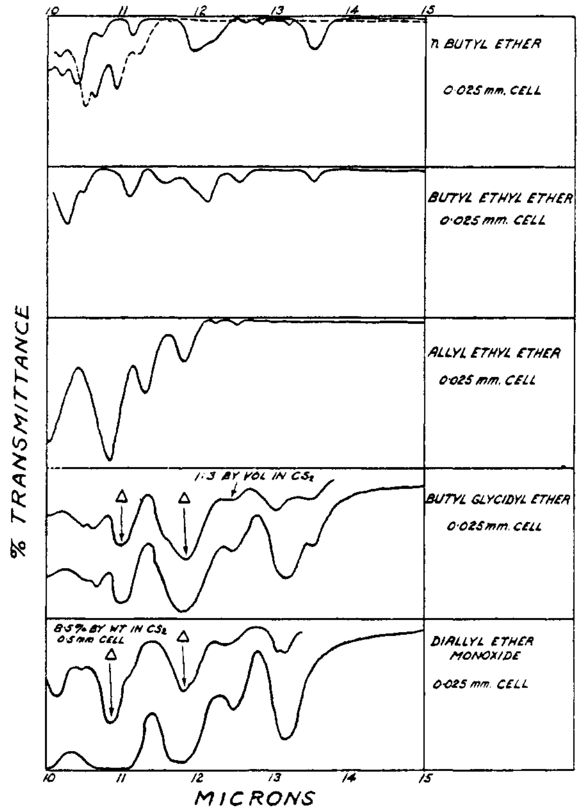

Figure 13. Spectra of Ethers

In Figure 14, all of the seven ethers as shown are the diluted samples in carbon disulfide to bring out more accurately the band positions. In all cases there are strong bands in the 11.0 and 11.8 micron positions. In diallyl ether dioxide the short wavelength band is at 10.96 microns (912 cm.$^{-1}$), shifted somewhat from the 10.86-micron band of the monoxide.

**Cyclic Oxides.** The four cyclic oxides were cyclohexene oxide, 4-vinylcyclohexene oxide (4-vinyl-1,2-epoxy cyclohexene), 4-vinylcyclohexene dioxide, and cyclohexadiene dioxide. The fifth compound is vinylcyclohexane oxide; while not a cyclic oxide, it is included here as it is useful in considering 4-vinylcyclohexene dioxide. It was a much more difficult problem to pick out probable epoxide bands because the vibrations of the carbon ring would be expected to be modified considerably and in this region of the spectrum the vibrations are strong. Thus reference hydrocarbons have been of little help. For the present it is intended only to point out which bands are common to the different compounds and therefore might be due to oxirane ring vibrations.

The spectra of the four cyclic oxides plus that of 4-vinylcyclohexane oxide are given in Figure 15. The most probable band attributable to an epoxide vibration is that at about 12.3 microns (813 cm.$^{-1}$) which is common to all the cyclic oxides; it is the most intense band of cyclohexadiene dioxide and shows least variation in position in the four compounds. This band does not appear in vinylcyclohexane oxide. The vinyl vibration at 11 microns in 4-vinylcyclohexene monoxide probably masks an epoxide band at this point. This could be the band at 10.81 microns (925 cm.$^{-1}$) in 4-vinylcyclohexene dioxide. However, such a band if present has been shifted in cyclohexene oxide to 11.22 microns (891 cm.$^{-1}$) and for reasons to be shown later would be the 10.69-micron (935 cm.$^{-1}$) band in cyclohexadiene dioxide. The band at 10.60 microns (943 cm.$^{-1}$) for vinylcyclohexane oxide is probably due to the oxirane ring, based upon the band intensity and a comparison with ethyl, propyl, and butyl cyclohexane (not shown). The logical choice of the second epoxide band in vinylcyclohexane monoxide is that at 11.93 microns (838 cm.$^{-1}$). However, it would possibly be expected that this band would appear in 4-vinylcyclohexene dioxide if due to the

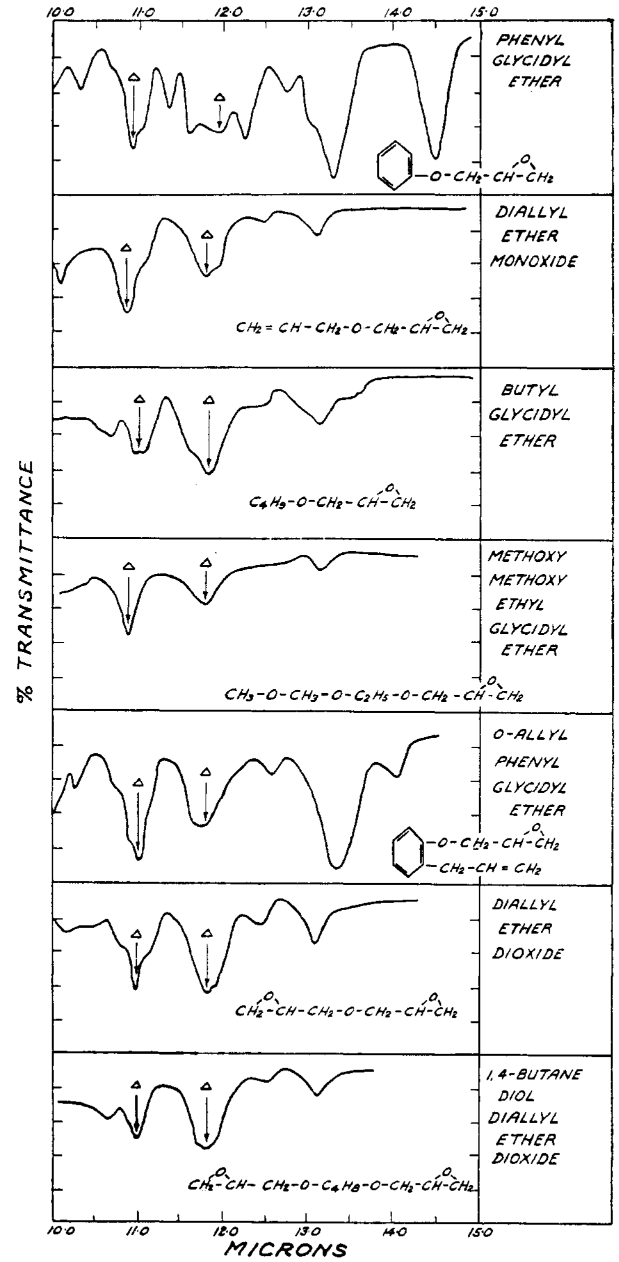

Figure 14. Spectra of Seven Ethers

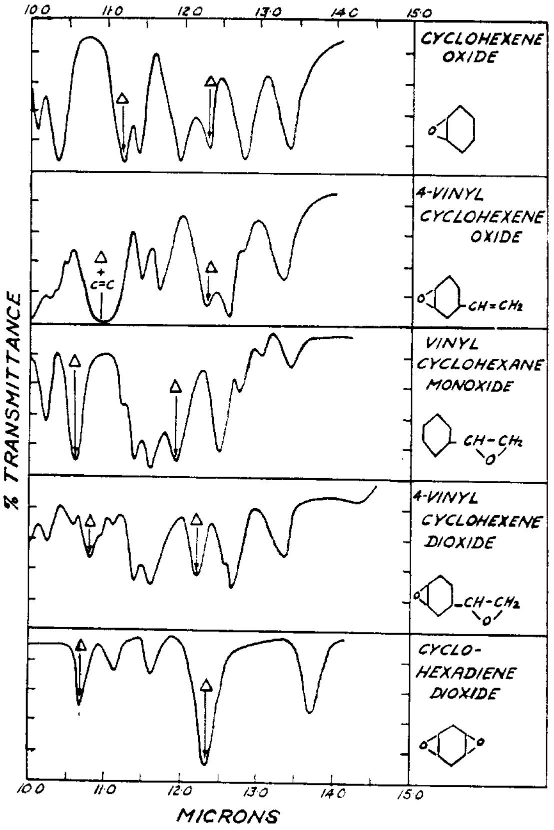

**Figure 15. Spectra of Cyclic Oxides**

epoxide, but it does not. A weak band in the latter corresponding to the 10.6-micron band of the former does appear but that is all. The strong band at 12.49 microns (801 cm.$^{-1}$) in vinylcyclohexane monoxide might be present in vinylcyclohexene dioxide as the side band at 12.54 microns (797 cm.$^{-1}$) in vinylcyclohexane-4-dioxide but the intensity is very low. In fact, there is no real indication that the probable epoxide bands of vinylcyclohexane monoxide do appear in this dioxide.

A comparison of the spectrum of cyclohexadiene dioxide with propene oxide as shown in Figure 16 is of considerable interest. Except for the addition of a small band in cyclohexadiene dioxide, the spectra are similar, although the bands of cyclohexadiene dioxide are shifted to longer wave lengths. It is the relationship between these spectra that indicates the choice of the 10.69-micron (935 cm.$^{-1}$) band in cyclohexadiene dioxide as an epoxide vibration. It may not be a coincidence that the molecule of cyclohexadiene dioxide can be considered as a ring formed by two molecules of propene oxide.

**Table of Bands.** In Table III are listed the probable epoxide bands as brought out by the preceding discussion. The proposed bands vary from 10.52 (950 cm.$^{-1}$) to 11.58 microns (863 cm.$^{-1}$) in the 11.0-micron position and from 11.57 (864 cm.$^{-1}$) to 12.72 microns (786 cm.$^{-1}$) in the 12-micron position, with the large majority of the bands at about 11.0 and 12.0 microns. As might be expected, there is less deviation in the position of the bands of the longer chain molecules. The substitution of a benzene ring on one of the oxide carbons shifts the bands to longer wave length as does the substitution of an α-methyl group. Except for *cis*- and *trans*-butene-2-oxides, all of the epoxide rings are at the terminal group. The geometric configuration does not appear to affect appreciably the 11-micron band, but it does affect the 12-micron band, the band for the cis configuration being at the longer wave length.

This is in line with the work of Shreve *et al.* (*8*) on the cis and trans isomers of long-chain fatty acids, esters, and alcohols where the bands of the cis configuration are at longer wave length than those of the trans compounds. However, they found only one band for each type, at 12 and 11.2 microns, respectively. In the majority of the epoxides, the band at the longer wave length is the more intense and it may be that the shorter wave-length band does not show up in these particular epoxides. This presupposes, however, a shift in the long wave-length band to a much shorter wave length than has been noted so far.

**Table III. Probable Epoxide Bands**

| Compound | About 11.0 Microns | | About 12 Microns | |
|---|---|---|---|---|
| | Microns | Cm.$^{-1}$ | Microns | Cm.$^{-1}$ |
| α-Methylstyrene oxide | 11.58 | 863 | 12.72 | 786 |
| Styrene oxide | 11.40 | 877 | 12.31 | 812 |
| Propene oxide | 10.52 | 950 | 12.09 | 827 |
| Isobutene oxide | 11.11 | 900 | 12.56 | 796[a] |
| *cis*-Butene-2-oxide | 11.29 | 886 | 12.87 | 777 |
| *trans*-Butene-2-oxide monoxide | 11.27 | 887 | 12.32 | 812 |
| Butadiene monoxide | 10.88 | 919 | 12.24 | 817 |
| Octene-1-oxide | 10.89 | 918 | 11.97 | 835 |
| Epichlorohydrin | 10.80 | 926 | 11.80 | 847 |
| Vinylcyclohexane oxide | 10.60 | 943 | 11.93 | 838 |
| Esters | | | | |
| Glycidyl butyrate | 10.98 | 911 | 11.71 | 854 |
| Glycidyl crotonate | 11.03 | 907 | 11.68 | 856 |
| Glycidyl sorbate | 11.01 | 908 | 11.57 | 864 |
| Glycidyl methacrylate | 10.99 | 910 | 11.86 | 843 |
| Glycidyl linoleate | 11.00 | 909 | 11.67 | 857 |
| Ethers | | | | |
| Phenyl glycidyl ether | 10.90 | 917 | 11.95 | 837 |
| Diallyl ether monoxide | 10.86 | 921 | 11.82 | 846 |
| Butyl glycidyl ether | 10.94 | 914[a] | 11.84 | 844 |
| Methoxy methoxy ethyl glycidy ether | 10.87 | 920 | 11.81 | 847 |
| *o*-Allyl phenyl glycidyl ether | 11.00 | 909 | 11.81 | 847 |
| Cyclic Oxides | | | | |
| Cyclohexene oxide | 11.22 | 891 | 12.31 | 812 |
| 4-Vinylcyclohexene oxide[b] | 10.93 | 915 | 12.31 | 812 |
| 4-Vinylcyclohexene dioxide | 10.81 | 925 | 12.22 | 818 |
| Cyclohexadiene dioxide | 10.69 | 935 | 12.34 | 810 |
| Dioxides | | | | |
| Butadiene dioxide | 10.92 | 916 | 11.48<br>12.34 | 871<br>810 |
| 1,4-Pentadiene dioxide | 10.93 | 915 | 11.80<br>12.06 | 847<br>829 |
| Diallyl ether dioxide | 10.96 | 912 | 11.81 | 847 |
| 1,4-Butanediol diallyl ether dioxide | 10.96 | 912 | 11.82 | 846 |

[a] First of double band.

[b] 4-Vinyl-1,2-epoxycyclohexane.

**Consistency of Chosen Bands with Reactivity Data.** Flett (*4*) has shown that in some cases there is a correlation between the position of a characteristic absorption band and the reactivity of the group. The reactivity depended on the type of substituent and whether it was electron-attracting or electron-donating. In general an electron-attracting substituent increased the frequency but this was not always the case. Data on the reactivity of 20 of the oxirane compounds with acetic acid were available. It was therefore of interest to plot these data against the chosen epoxide bands.

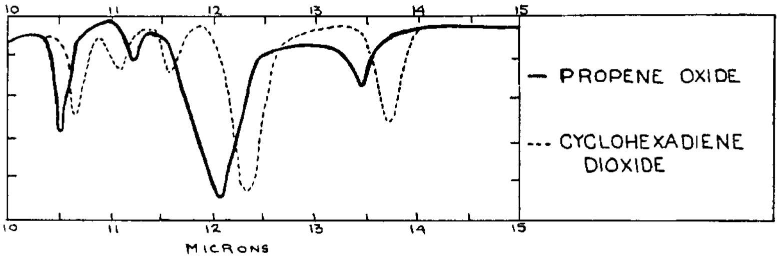

**Figure 16. Spectra of Cyclohexadiene Dioxide and Propene Oxide**

In Figure 17, the "reactivity" at 25° C. is plotted for a number of the oxirane compounds. Considering the wide range of reactivities, the correlation of the chosen bands is good. This is indicated by the two retrogressive curves which are drawn for each set of points. These were derived from retrogressive equations calculated by the method of Snedecor (*9*). The equations used, which are based on fourteen values each of $X$ and $Y$, are as follows:

Left-hand curves, Figure 17:

$$\text{Log } \hat{Y} = -35.9496 + 3.187\, X$$

$$\hat{X} = 11.1018 + 0.1428 \log Y$$

Right-hand curves, Figure 17:

$$\hat{Y} = -50.3463 + 4.073\, X$$

$$\hat{X} = 12.3202 + 0.2063 \log Y$$

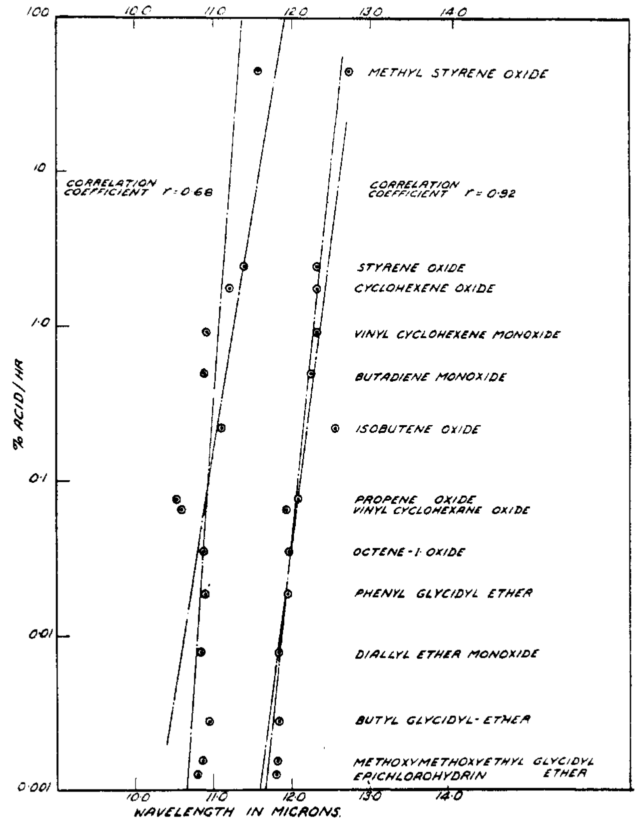

**Figure 17. Relation of Reactivity at 25° C. to Wave Length of Absorption Bands**

The respective correlation coefficients are 0.68 and 0.92, which are significant at the 1% level—that is, correlation coefficients as great as this would be expected less than once in 100 times for sets of $X$'s and $Y$'s which were not related.

The reactivity data for the esters at 40° C. are given in Figure 18, along with those for *cis*- and *trans*-butene-2-oxides. Measurements at 25° C. were not available for the butene-2-oxides and there was a bigger spread in reactivity data for the esters at 40° C. than at 25° C. The short wave-length bands of the esters are consistent with those of Figure 17, but the bands at longer wave lengths are not. The dashed line corresponds with the general slope of the long wave-length series of points. The bands fall to the left of this line and tend to slope in the opposite direction.

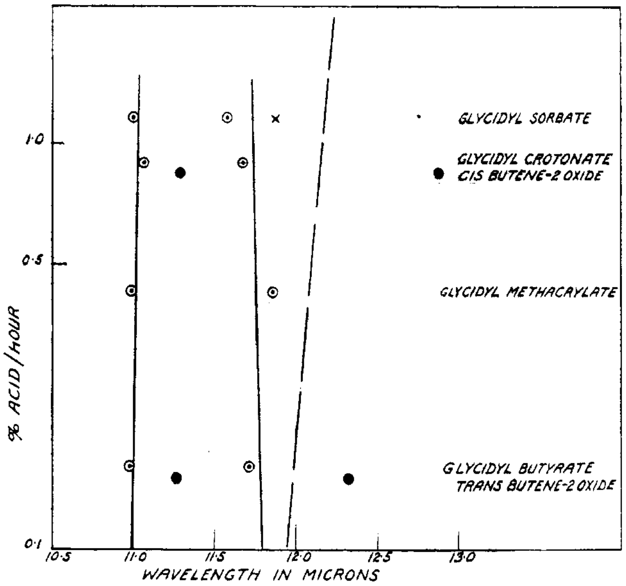

**Figure 18. Relation of Reactivity at 40° C. to Wave Length of Absorption Bands**

Using the 11.88-micron band of glycidyl sorbate and the 11.93-micron band of glycidyl crotonate, a line could be drawn with the same slope as the dashed line. However, it has already been shown that the 11.67-micron band of the crotonate is probably due to the epoxide vibration. Using the sorbate 11.88-micron band with the other bands the same, the line would be vertical and indicate no change of band position with reactivity. This reversal of slope is disturbing in the esters. The epoxide bands of *cis*- and *trans*-butene-2-oxides do not fall on any of the curves. However, there is general agreement in that the long wave-length band of the trans isomer is at a shorter wave length in line with its lower reactivity. Isobutene oxide has about the same reactivity as that of the *cis*-butene-2-oxide at 40° C., 0.89 as against 0.85, and the position of the long wave-length band at 12.61 microns would be in agreement with the 12.87-micron band of the *cis*-butene-2-oxide. No correlation statistics were made on these points because of the restricted reactivity range.

The results indicate some relationship between reactivity and wave-length position. Deviations, however, indicate that other factors enter into this correlation. This may be in the relative intensity of the bands, which has not been considered here. A point which also needs resolving is whether both or only one of the epoxide bands is connected with the reactivity of the compound.

## GENERAL CONCLUSIONS

Strong infrared absorption bands have been found in the spectra of oxirane compounds from 10 to 13 microns. The intensity of these bands, their appearance at restricted regions of the spectra in molecules of widely differing structures, and lack of interference from similar bands in related saturated and unsaturated derivatives are evidence that they are characteristic of the oxygen ring.

In general, the positions of the designated epoxide bands show a correlation with the reactivities of the oxirane compounds with acetic acid but no conclusions as to the significance of this have been attempted.

## ACKNOWLEDGMENT

The author wishes to express his thanks to Anne Pink, who did most of the work in transforming the original spectra to per cent transmittance, to D. Z. Robinson for permission to publish his results on the 8-micron epoxide band, and to A. W. Birnie who made the statistical calculations for Figure 17.

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# Analysis of Binary Solvent Mixtures of Conducting Solutions by a Radio-Frequency Method

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**A method has been developed for the analysis of binary solvent mixtures containing considerable electrolyte. Commonly available radio-frequency instruments and conventional conductance apparatus may be used. The method is based upon the relation of the high-frequency capacitance of an insulated cell to the conductance and dielectric constant of the solution within the cell. For the system dioxane-water-potassium chloride, in the range of conductance for which the method is applicable it is shown that the dielectric constant of the solvent mixture can be determined within 0.3 dielectric constant unit. The dielectric constant can be related directly to the composition of the binary mixture. The method may be extended to any similar system and within certain limits calibration curves based upon one system may be used for analysis of similar systems.**

THE purpose of this article is to show that the composition of a binary solvent mixture, having considerable conductance, may be found from an indirect determination of the dielectric constant of the solvent mixture. This is accomplished through the measurement of the ordinary conductance of the solution and the radio-frequency capacitance of an insulated cell containing the solution. It is presented as an empirical method for finding the dielectric constant which the solvent would have in the absence of electrolyte. The conductance and high-frequency apparatus used are now available in many analytical laboratories or are readily obtained commercially. The type of insulated cell which has been commonly used for high-frequency work is very convenient for this empirical method but is not suitable for the evaluation of constants which would permit more fundamental calculations such as the dielectric constant of the solution (solvent plus solute). The method as presented here makes use of the General Radio Twin-T impedance-measuring circuit and a Leeds & Northrup Co. conductance apparatus but similar methods could be worked out using other radio-frequency and audio-frequency equipment.

It has been demonstrated adequately that radio-frequency oscillators may be used to measure the dielectric constants of liquids contained in insulated cells. Fischer (*5*), in 1947, showed that the dielectric constant of the liquid contained in a glass vessel which was placed within the inductance coil of a crystal oscillator could be related by a simple calibration curve to the position of the tuning capacitor at which oscillation was initiated.

Consideration of the simple equivalent circuit presented by Blaedel *et al.* (*1*) and discussed in detail by Hall (*6*), Blaedel, Malmstadt, Petitjean, and Anderson (*2*), and Reilley and McCurdy (*8*) shows that such a relationship should be expected. In 1950, West, Burkhalter, and Broussard (*10*) showed, for an instrument based upon a beat-frequency oscillator, that various pure organic liquids produced characteristic beat frequencies. Their cell arrangement and the principles involved were similar to those of Fischer (*5*), although they did not relate the beat frequencies produced by the organic liquids to the dielectric constants of the liquids. For liquids of slight conductivity such as the pure organic liquids just mentioned, and including the liquid mixtures studied by West, Robichaux, and Burkhalter (*11*) and by West, Senise, and Burkhalter (*12*), it has been the present authors' experience that the data for all such systems may be plotted as one smooth curve relating dielectric constant to instrument response. The present article extends this type of determination to liquids having appreciable conductance.

Measurements in the direct-reading range of the Twin-T impedance-measuring circuit (*9*) are limited to admittances with low conductance components; the exact limit is proportional to the frequency. The range of this bridge can be extended by connecting the unknown admittance in series with an auxiliary capacitor of such magnitude that the net admittance of the combination falls within the direct-reading range of the Twin-T circuit. From a measurement of the net admittance of the combination and a measurement of the auxiliary capacitor alone, the unknown impedance can be calculated by use of the equations:

$$R = \frac{G}{G^2 + \omega^2C^2} \tag{1}$$

$$X = \frac{\omega C}{G^2 + \omega^2C^2} \tag{2}$$

where $R$ is the series equivalent resistance and $X$ is the series equivalent capacitive reactance of the admittance. $G$ is the conductive component of the admittance and $C$ is the capacitance as measured by the bridge. $\omega$ is $2\pi$ times the frequency.

The unknown resistance, $R_x$, and the unknown reactance, $X_x$, are then given by:

$$R_x = R_1 - R_2 \tag{3}$$

$$X_x = X_1 - X_2 \tag{4}$$