

# Ozonolysis of Epoxidized Natural Rubber

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## Synopsis

The epoxidized natural rubber was fragmented by ozonolysis and the ozonolyzed mixture was analyzed by gas chromatography/mass spectroscopy. The peak areas of the analyzed partial chromatograph were used to calculate the ratio of CC, CEC, and CEEC (dyad, triad, and tetrad) compared with the theoretical value calculated assuming random epoxidation of the latex. In this manner the epoxidation reaction was proved to be random.

## INTRODUCTION

Epoxidation of natural rubber and other unsaturated elastomers is well known.<sup>1-3</sup> Some properties of natural rubber such as oil resistance, air permeability, and abrasion resistance are found to be improved by epoxidation.<sup>4</sup> Even though natural rubber could be epoxidized in solution, only the latex method using performic acid was found to be economical.<sup>5</sup> As a result there has been a great deal of interest, recently, in the epoxidation of natural rubber latex.

It is important to determine whether the monomer sequence distribution is indicative of random epoxidation of double bonds on treatment of natural rubber in the latex with peracids. <sup>13</sup>C NMR<sup>6</sup> and other<sup>7,8</sup> investigations have indicated that epoxidation of natural rubber latex is random. However, an electron microscopic study of latex, tracing the changes that occurred in the latex particle during epoxidation, showed a characteristic "ringed" structure that appeared around the epoxidized latex particles.<sup>9</sup> This was interpreted to indicate that the epoxidation of natural rubber proceeds in a manner related to the heterodispersibility of the latex. Thus, at any instant, the whole epoxidized natural rubber latex is thought to consist of a range of particles of different epoxidation levels. This paper describes an ozonolysis study to confirm our earlier observation<sup>6</sup> that the epoxidation is random in natural rubber latex.

## EXPERIMENTAL

### Materials

Solid natural rubber (Latex Crepe IX) and centrifuged natural rubber latex (60% dry rubber content, ammonia stabilized) were obtained from Sri Lanka. Solvents and hydrogen peroxide (27.5% w/w) were analytical reagents and

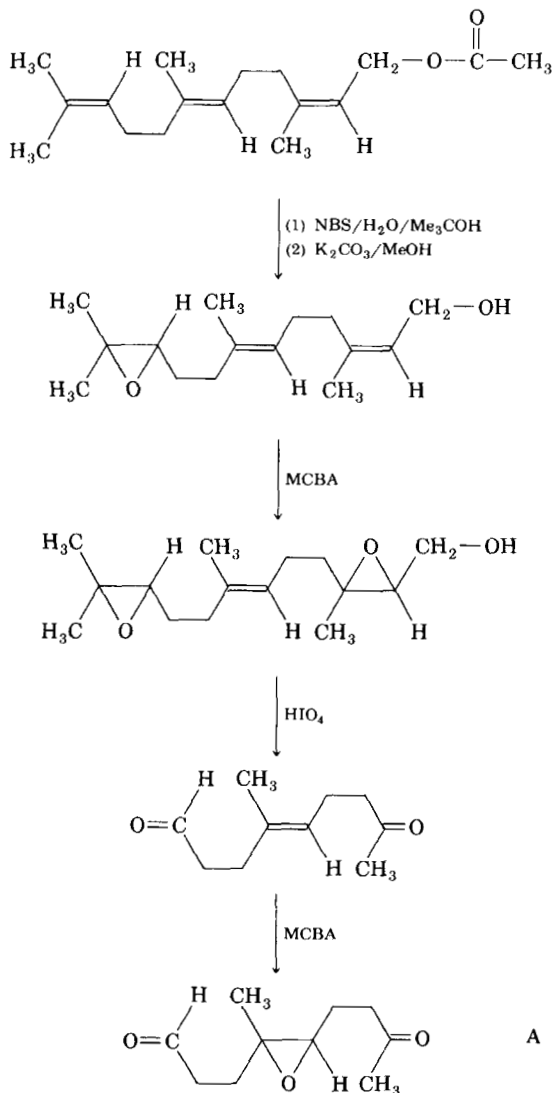
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*m*-chloroperbenzoic acid, and dimethyl sulfoxide were technical grades obtained from Aldrich Chemical Company. Farnesyl acetate was obtained from Fluka AG, Switzerland.

### Methods

#### *Epoxidation of Natural Rubber and Farnesyl Acetate*

Natural rubber was epoxidized either in solution<sup>10</sup> or in latex.<sup>5,6</sup> The epoxidized rubber was purified by redissolving in chloroform and reprecipitation. Farnesyl acetate was epoxidized stereospecifically<sup>11</sup> and also using *m*-chloroperbenzoic acid (MCBA) to achieve the product shown in Scheme 1.



Scheme 1.

### *Periodic Acid Degradation of Epoxy Groups*

A solution containing periodic acid in tetrahydrofuran (THF) was prepared by stirring the required amount of the powdered periodic acid with THF for 1 h. To a solution of epoxidized compound (20% w/v) in THF cooled in a cold water bath, the stoichiometric amount of the periodic acid solution was added dropwise over a 1 h period under nitrogen. The milky reaction mixture was stirred until the solution became almost clear and the white precipitate of iodic acid was separated out. The solution was then filtered and the solvent removed.

### *Ozonolysis of Epoxidized Natural Rubber*

The epoxidized natural rubber (0.1 g) was dissolved in 15 mL of analytical grade dichloromethane. Ethanol (5 mL) was added to the solution. Ozonized oxygen ( $400 \text{ mL min}^{-1}$ ), generated by the Wallace and Tuman ozonator at 200 V, was bubbled into these solutions at  $-78^\circ\text{C}$ . As some of the epoxidized natural rubbers were insoluble, they needed an extended reaction time. The dichloromethane was then evaporated in a stream of  $\text{N}_2$  at room temperature. Dimethyl sulfide (1.26 g) in ethanol/water was added and the solution left overnight at room temperature.

### *Thin Layer Chromatographic Separation of the Ozonolysis Product*

The residue obtained from ozonolysis of the epoxidized rubber was applied to a silica gel plate (thickness 0.4 mm) and developed with hexane/ethyl acetate (80:20 v/v). After developing, the silica gel above 1 cm from the base line was scraped off from the plate, extracted with ethyl acetate, and filtered. Finally the ethyl acetate was evaporated. This procedure removed the highly immobile polymeric material from the lower molecular weight ozonolysis products.

### *Gas-Liquid Chromatography/Mass Spectra*

The solution to be analyzed ( $1 \mu\text{L}$ ) was injected directly into a  $3.7 \text{ m} \times 6 \text{ mm}$  GC column (10% carbowax 20 m on 44-60 mesh Embagel) attached to a Packard 878 gas chromatograph equipped with an ionization detector. Inlet, outlet, and column temperatures were maintained at  $150^\circ\text{C}$  with  $\text{N}_2$  as carrier gas flowing  $40 \text{ mL/min}$ . A solution of the nonpolymeric ozonolysis product separated by TLC was used in GC/MS under similar conditions.

## RESULTS AND DISCUSSION

In the epoxidized natural rubber the epoxidized and unepoxidized isoprene units were denoted by E and C, respectively. The dyad, triad, and tetrad sequences between these isoprene units were denoted by, for example, CC, CEC and CEEC, respectively.<sup>6</sup>

### **Fragmentation of Farnesyl Acetate**

Farnesyl acetate was first epoxidized using a stereoselective method<sup>11</sup> as shown in Scheme 1. This results in 10,11-epoxy farnesol which was epoxidized

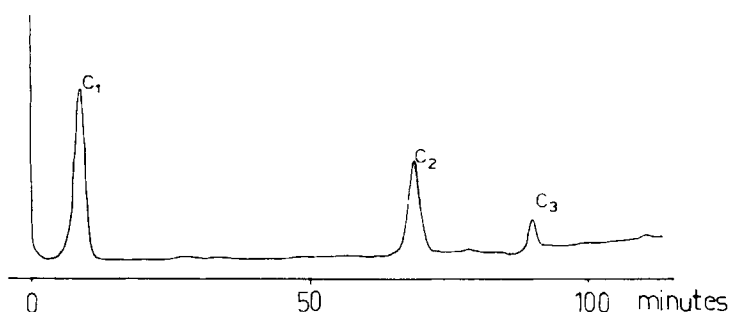


Fig. 1. Gas chromatograph of the product obtained by ozonolysis of epoxidized (reduced) natural rubber.

using MCBA. The hydroxyl group has a directive effect which leads to the epoxidation of the other terminal double bond.<sup>12</sup> The resulting diepoxy farnesol (with both terminal double bonds epoxidized) was then cleaved using periodic acid and the remaining double bond was epoxidized with MCBA. The compound (4,5-epoxy-8-oxononanal) that results from this series of reactions is shown in Scheme 1 and is called compound A in the text.

### Fragmentation of Epoxidized Natural Rubber

The product obtained by ozonolysis of epoxidized natural rubber (after reduction with dimethyl sulfide) was chromatographed, and the resultant chromatograph is shown in Figure 1. The peak  $C_1$  was identified as laevulinaldehyde by comparison with the product obtained by the ozonolyzed natural rubber.<sup>13</sup> The peaks  $C_2$  and  $C_3$  were identified as being due to compound A, as obtained from the fragmentation of farnesyl acetate. These are the two smallest molecular weight compounds expected from the ozonolysis of epoxidized natural rubber (see Table I), that is, the fragmented portion of the CC dyad (laevulinaldehyde) and CEC triad (compound A of Scheme 1). Analysis of the rest of the peaks in the complicated chromatograph was difficult. To overcome this difficulty, the low molecular weight products of the ozonolyzed, epoxidized natural rubber mixture, which was initially separated on a TLC

TABLE I  
The Expected Products from Various Sequences of Epoxidized and Unepoxidized Isoprene Units

Sequence	Fragment structure	No. of carbon atoms
CC	$\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$	5
CEC	$\text{HC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{O}}{\text{C}}}-\text{CH}-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$	10
CEEC	$\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{O}}{\text{C}}}-\text{CH}-\text{CH}_2-\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{O}}{\text{C}}}-\text{CH}-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$	15

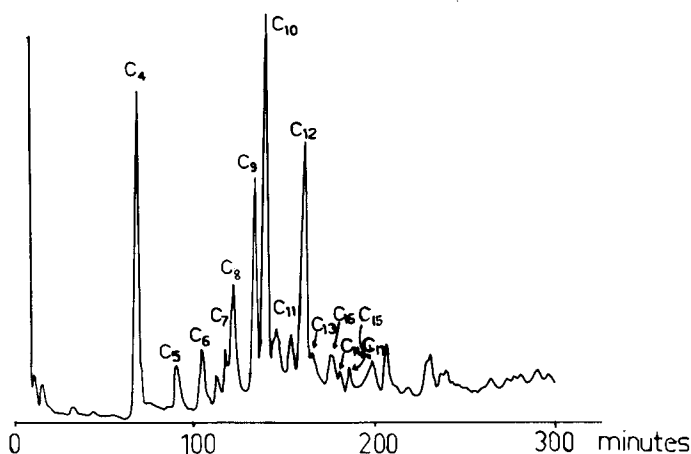
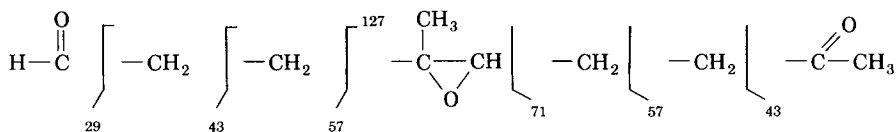


Fig. 2. Gas chromatograph of low molecular weight products of ozonolyzed epoxidized natural rubber.

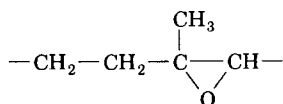
plate from its polymeric fragments, were analyzed using GC/MS. The resultant gas chromatograph is shown in Figure 2, and the assigned structures are shown in Table II. The initial TLC separation was necessary to prevent any polymeric material entering and blocking the columns. The peak due to laevulinaldehyde was not present, having probably been evaporated from the mixture due to its high volatility.

### Identification of Peaks C<sub>4</sub>, C<sub>5</sub>, and C<sub>6</sub>

All three compounds exhibited very similar mass spectra. The mass spectrum of C<sub>4</sub> is shown in Figure 3, and this compound has a molecular ion at  $m/e$  184. The spectra of C<sub>5</sub> and C<sub>6</sub> are very similar so that these peaks must be due to various stereoisomers of the product A (Scheme 1). Fragmentation of this molecular ion gives rise to the daughter ions as shown below:



as well as the fragment

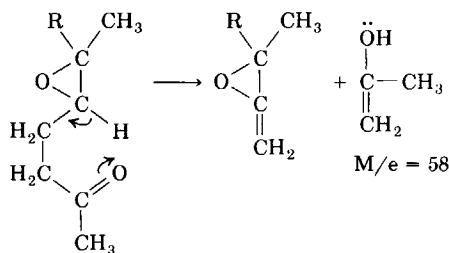


at  $m/e$  84. The McLafferty rearrangement with  $\beta$ -cleavage is not possible from the aldehyde end of the molecule as there is no H, but this rearrange-

TABLE II  
Analysis of the Gas Chromatograph of Ozonized Epoxidized Natural Rubber

Peak	Scan time (min)	Molecular weight	No. of carbon atoms	Structure proposed
C <sub>1</sub>	8	100	5	$\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$
C <sub>4</sub>	69	184	10	$\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{O}}{\text{C}}}-\text{CH}-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$
C <sub>5</sub>	91			
C <sub>6</sub>	105			
C <sub>7</sub>	118	166	10	$\begin{array}{c} \text{HC}-\text{CH}_2-\text{CH}_2-\text{CH} \\   \quad   \quad   \\ \text{HC}-\text{O}-\text{C}-\text{C}-\text{O}-\text{C} \\   \quad   \quad   \\ \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \end{array}$
C <sub>8</sub>	122			
C <sub>9</sub>	134	200	10	$\begin{array}{c} \text{H}_2\text{C}-\text{CH}_2-\text{H}_2\text{C}-\text{CH}_2 \\   \quad   \quad   \quad   \\ \text{O}=\text{C}-\text{O}-\text{C}-\text{CH}-\text{C}-\text{CH}_3 \\   \quad   \quad   \\ \text{CH}_3 \quad \text{OH} \quad \text{O} \end{array}$
C <sub>10</sub>	140			
C <sub>11</sub>	154			
C <sub>12</sub>	161	250	15	$\begin{array}{c} \text{HC}-\text{CH}_2-\text{H}_2\text{C}-\text{CH}_2-\text{H}_2\text{C}-\text{CH} \\   \quad   \quad   \quad   \quad   \\ \text{HC}-\text{O}-\text{C}-\text{CH}-\text{O}-\text{C}-\text{CH}-\text{O}-\text{C}-\text{CH}_3 \\   \quad   \quad   \quad   \\ \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \end{array}$
C <sub>13</sub>	166			
C <sub>14</sub>	182			
C <sub>15</sub>	186			
C <sub>16</sub>	177	282	15	$\begin{array}{c} \text{H}_2\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{H}_2\text{C}-\text{CH} \\   \quad   \quad   \quad   \quad   \\ \text{O}=\text{C}-\text{O}-\text{C}-\text{C}=\text{O}-\text{C}-\text{CH}-\text{O}-\text{C}-\text{CH}_3 \\   \quad   \quad   \\ \text{CH}_3 \quad \text{O} \quad \text{HO} \quad \text{CH}_3 \end{array}$
C <sub>17</sub>	198	266	15	$\begin{array}{c} \text{H}_2\text{C}-\text{CH}_2-\text{H}_2\text{C}-\text{CH}_2-\text{H}_2\text{C}-\text{CH} \\   \quad   \quad   \quad   \quad   \\ \text{O}=\text{C}-\text{O}-\text{C}-\text{CH}-\text{O}-\text{C}-\text{CH}-\text{O}-\text{C}-\text{CH}_3 \\   \quad   \quad   \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$

ment can occur from the ketoterminal as in Scheme 2:



Scheme 2.

The compound can also undergo several scissions because of the epoxide group. Thus, in Scheme 3 hydrogen rearrangement with concomitant fission of the bond connecting the oxygen atom to the carbon atom yields an inter-

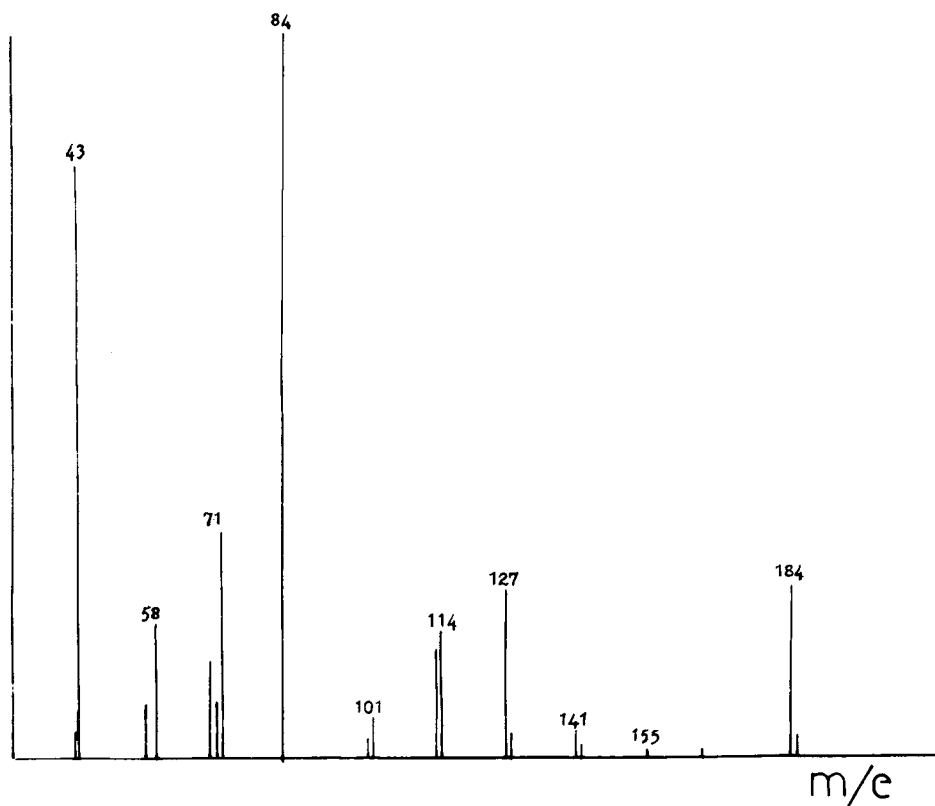


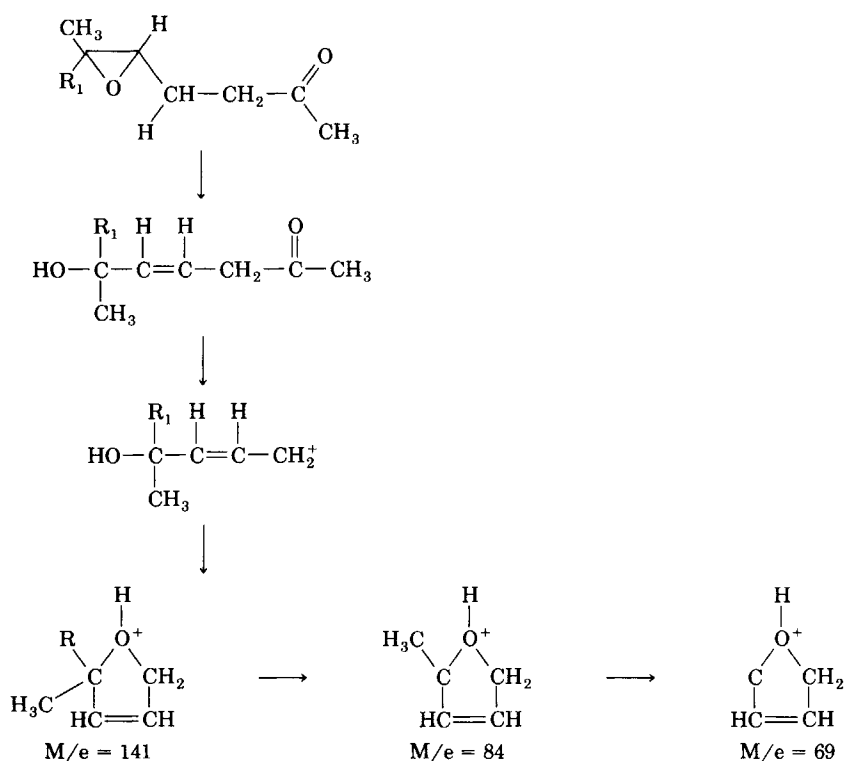
Fig. 3. Mass spectrum of peak  $C_4$  from Figure 2.

mediate which can undergo subsequent allylic cleavage. Similar scission from the aldehyde group produces fragments of  $m/e$  155 and 84.

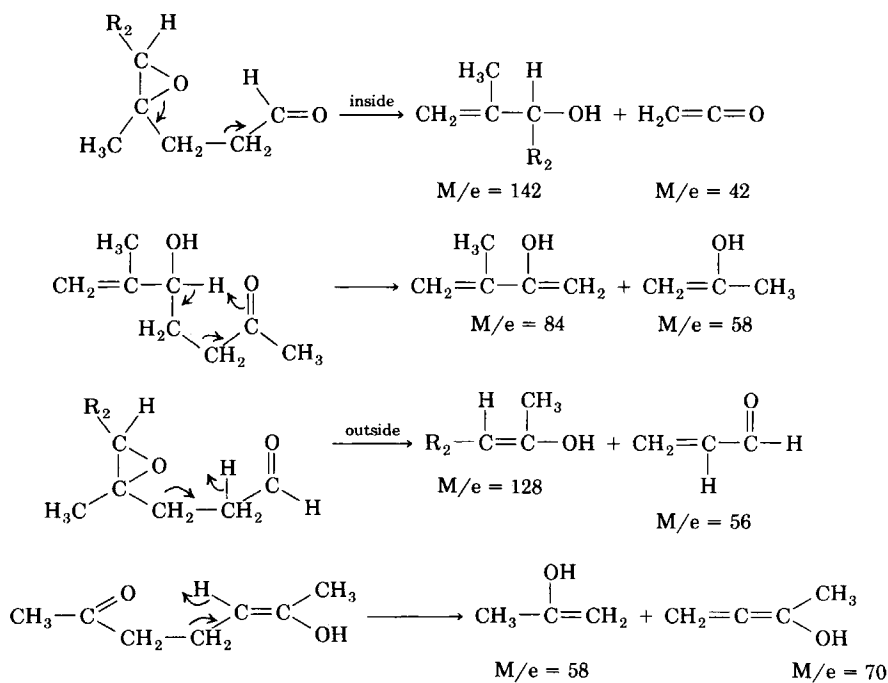
A study<sup>14</sup> with simple epoxyalkanes has shown that both internal as well as external McLafferty rearrangements can occur and that the charge may be retained on either the oxygen containing species or the olefin moiety (Scheme 4). In the case of compound A only the external rearrangement is possible (from the keto-end) giving fragments at  $m/e$  70, 114, and further breakdown is not possible.

Epoxides are known to undergo transannular cleavages, but evidence exists that such double bond fission is usually accompanied by a rearrangement process.<sup>14</sup> The corollary of this statement is that ionized carbene species are not favored in electron impact induced fragmentations.<sup>14</sup> In the light of these conclusions, it seems reasonable to propose that all transannular cleavages of aliphatic epoxides must proceed with hydrogen rearrangement (Scheme 5), although, in those cleavages leading to ions of even mass, such rearrangements would not be detected.

As a result of the various fragmentations discussed above, the following daughter ions were expected in the mass spectra; at  $m/e$  29, 42, 43, 56, 58, 69, 70, 71, 84, 100, 101, 113, 114, 127, 128, 141, 142, 155, and 184. The appearance of these peaks in the mass spectra, confirmed that the peaks  $C_4$ ,  $C_5$ , and  $C_6$  in

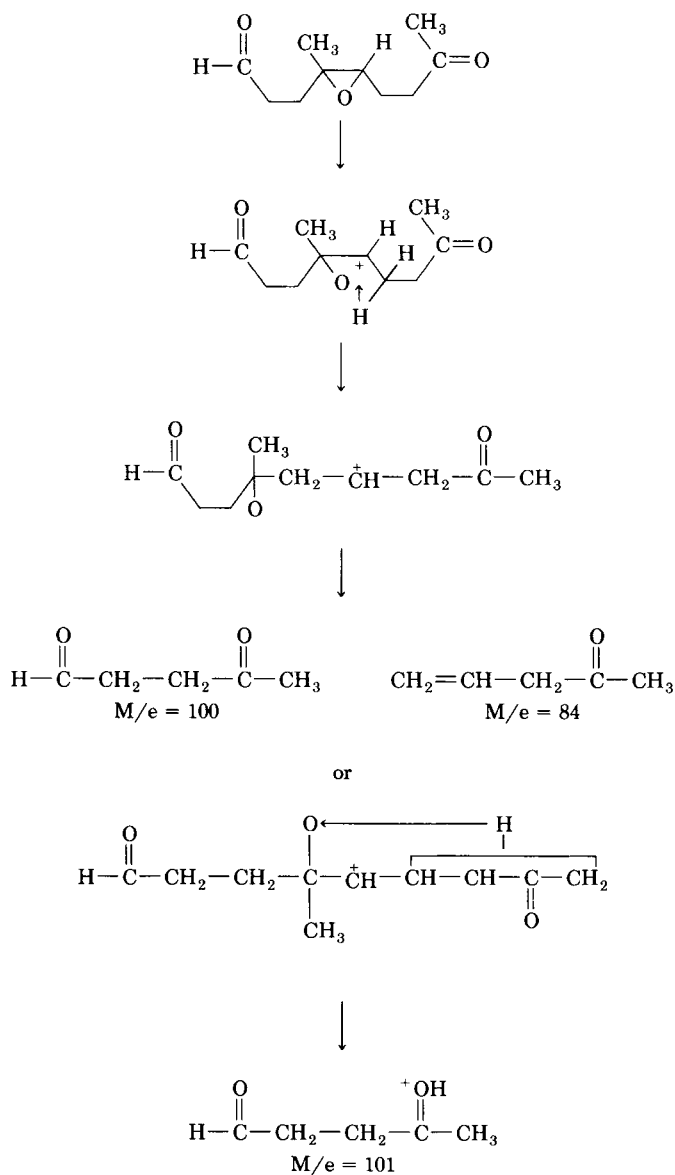


Scheme 3.



Scheme 4.





Scheme 5.

the chromatograph were due to the compound with structure A (Scheme 1). The several peaks must be due to different stereoisomers of this product.

### Identification of Peaks C<sub>7</sub> and C<sub>8</sub>

The mass spectra corresponding to these two peaks were very similar and are illustrated in Figure 4 (for C<sub>7</sub>). Both exhibited molecular ions at  $m/e$  166. The type of fission shown in Scheme 6 is predicted in ozonides<sup>15</sup> which will account for the formation of a compound with molecular weight of 166.

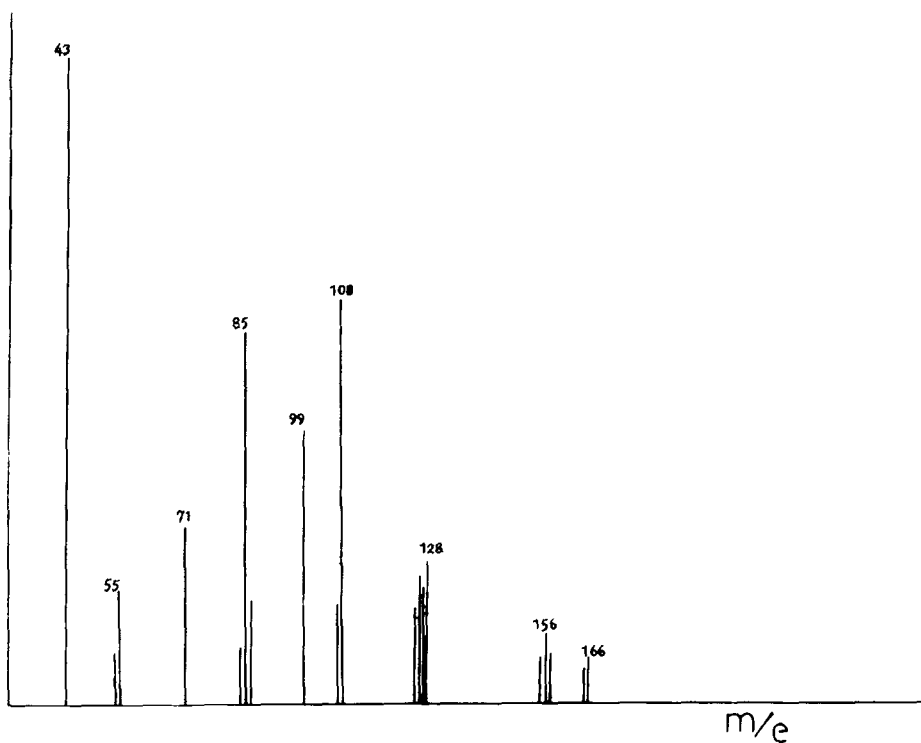


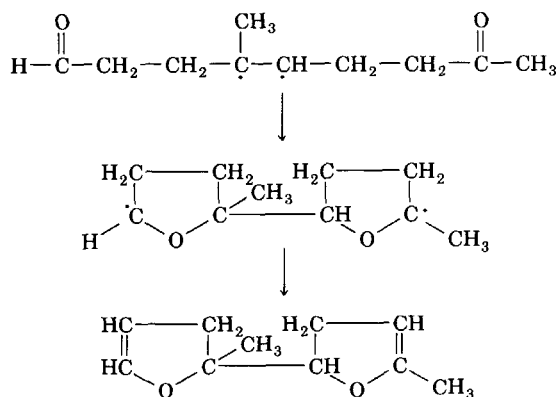
Fig. 4. Mass spectrum of peak C<sub>7</sub> from Figure 2.

#### Identification of Peaks C<sub>9</sub>, C<sub>10</sub> and C<sub>11</sub>

The mass spectrum is shown in Figure 5 and the molecular peak is  $m/e = 200$ . It is possible by mass spectroscopy to segregate the 5, 10, and 15 carbon atom fragments.

#### Identification of Peaks C<sub>12</sub>, C<sub>13</sub>, C<sub>14</sub>, and C<sub>15</sub>

The mass spectrum is shown in Figure 6. The compound has a molecular ion at  $m/e = 250$ , but it is not possible to propose a reaction scheme to account for this outcome.



Scheme 6.

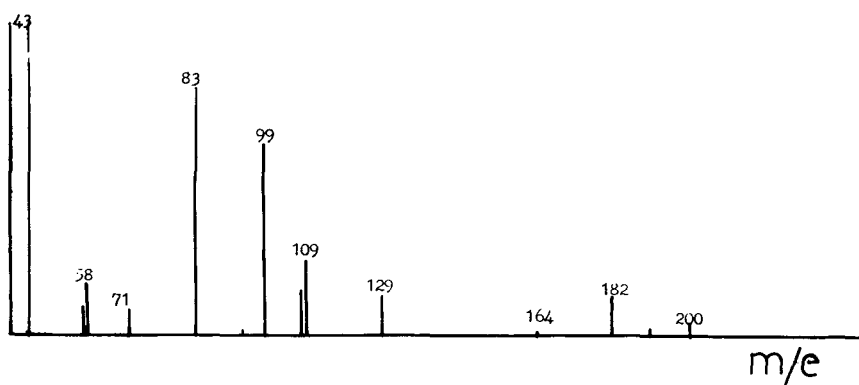


Fig. 5. Mass spectrum of peak  $C_9$  from Figure 2. The mass spectra of  $C_{10}$  and  $C_{11}$  is similar.

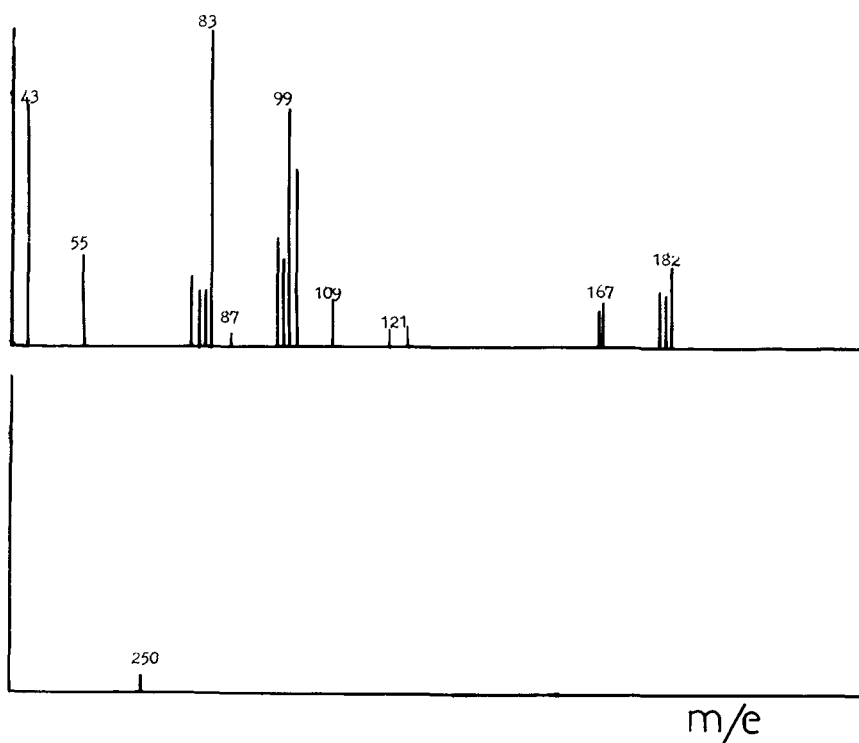


Fig. 6. Mass spectrum of peak  $C_{12}$  from Figure 2. The mass spectra of  $C_{13}$ ,  $C_{14}$ , and  $C_{15}$  are similar.

Even though the precise structure of the components giving rise to the peaks in the chromatograph may be in doubt, the peaks could invariably be identified as arising from compounds with 5, 10, and 15 carbon atoms. These are related to the CC, CEC, and CEEC (dyad, triad, and tetrad), respectively.

#### Microstructure of Epoxidized Rubber

The chromatographs could be used to carry out a quantitative analysis of the product. It is clear that during the TLC separation process the

TABLE III  
The Ratio of CC/ECE/CEEC Units in the Epoxidized Natural Rubber

Level of epoxidation	20%	30%	40%	50%	60%
Value calculated using chromatographs for latex epoxidized rubber	25.1; 5.16; 1	11.0; 3.35; 1	6.30; 2.51; 1	3.97; 1.99; 1	2.85; 1.70; 1
Value calculated using chromatographs for solution epoxidized rubber	25.8; 5.12; 1	11.7; 3.84; 1	6.37; 2.54; 1	3.96; 2.00; 1	2.80; 1.70; 1
Value calculated theoretically	25.6; 5.12; 1	11.1; 3.34; 1	6.31; 2.52; 1	3.96; 1.98; 1	2.80; 1.68; 1

laevulinolaldehyde (the smallest fragment expected) evaporated due to its high volatility. As some new peaks appeared after the TLC separation process, both chromatographs had to be used in the quantitative analysis. The two chromatographs could be standardized using the common peak at retention time 69 min. The chromatograph peak areas could be used to calculate the ratio of CC/CEC/CEEC (dyad, triad and tetrad) by combining the peaks due to compounds containing 5, 10, and 15 carbon atoms. These results, compared with the values calculated assuming random epoxidation, are shown in Table III for rubbers epoxidized to 20, 30, 40, 50, and 60%. The values for solution epoxidized rubber are also given for comparison in the table. It is clear that the calculated and experimental values agree well, within experimental error. Thus the evidence presented here confirms the previous observation that the epoxidation of natural rubber latex is random.

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