Electron-Impact Mass Spectrometry for Location of Epoxide Position in Long Chain *vic*-Dialkyl and Trialkyl Epoxides

B.A. BIERL and **MORTON BEROZA**, Organic Chemicals Synthesis Laboratory,
Agricultural Environmental Quality Institute[1], Beltsville, Maryland 20705

ABSTRACT

Plots of percent abundance vs m/e for selected series of ions (differing by 14 mass units) obtained by low resolution mass spectrometry allowed the epoxide position to be located in 30 C_{17}-C_{21} *vic*-dialkyl and trialkyl epoxides. Major diagnostic fragmentations are as follows. In the *vic*-dialkyl epoxides of the study, fragments useful for determining epoxide position result from α-cleavage, and epoxide position may be recognized by the maxima obtained in a plot of percent abundance vs m/e values in the $C_nH_{2n-1}O$ series (113, 127, 141....); a similar plot of percent abundances vs m/e values in the C_nH_{2n-2} series (110, 124, 138....) also shows maxima for ions corresponding to those obtained by transannular cleavage plus water elimination. In the trialkyl epoxides, fragments most useful for locating epoxide position are those obtained from ions corresponding to α-cleavage plus H-transfer; epoxide position may, thus, be recognized by the maxima obtained in a plot of percent abundance vs m/e values in the $C_nH_{2n}O$ series (72, 86, 100....). Transannular cleavage with H-transfer produces $C_nH_{2n+1}O$ products (m/e 115, 129, 143....), with the fragment containing the methyl substituent being much more abundant.

INTRODUCTION

Epoxides are found in a variety of natural products, including oils, insect juvenile hormones, terpenes, and insect sex attractants. Bierl, et al., (1) summarized methods of identifying epoxides and reported means of recognizing these groups by gas chromatography (GLC) (2) and thin layer chromatography (TLC) (1). They also devised a method of locating epoxide position and configuration (1). More and better methods of elucidating the structure of epoxides are needed, particularly of natural products that are obtainable only in very small amounts. The present study reports an evaluation of electron-impact mass spectrometry as a means of locating epoxide position in some long chain aliphatic epoxides.

The fragmentation patterns of aliphatic epoxides in electron-impact mass spectrometry were described by Brown, et al. (3), Budzikiewicz, et al. (4), and Aplin and Coles (5). Our work extends these interpretations to higher mol wt branched and unbranched *vic*-dialkyl and trialkyl epoxides and describes other cleavage processes useful in the structure determination of these compounds.

Fragmentation of alkyl epoxides is characterized by α-,β-, and γ- cleavages to give C_nH_{2n+1} and $C_nH_{2n-1}O$ products. In low resolution mass spectrometry, as used in this study, a distinction between the two classes of fragments cannot be made, since both have masses fitting in the series m/e 43, 57, 71, 85.... Transannular cleavage, which also occurs, produces fragments of C_nH_{2n} (m/e 56, 70, 84....), $C_nH_{2n}O$ (m/e 58, 72, 86....), and $C_nH_{2n+1}O$ (m/e 59, 73, 87....). Usefulness of these fragmentation patterns for determination of epoxide position was explored by analysis of data from 30 C_{17}-C_{21} monoepoxides, most of which had 1 or 2 methyl or ethyl branches along the chain. For each mass series, i.e. series with masses differing by 14 mass units, for $-CH_2-$, the percent abundance observed for a given compound decreases with increasing m/e, unless there is a structural feature of the compound that produces a preferred fragmentation; these preferred fragmentations can be used to determine epoxide position.

TABLE I

Compounds analyzed

Compound number	Compound
1	7,8-epoxy-2-methyloctadecane
2	7,8-epoxy-2-methylhexadecane
3	7,8-epoxy-2-methylheptadecane
4	7,8-epoxy-2-methylnonadecane
5	7,8-epoxy-2-methyleicosane
6	2,3-epoxy-2-methyloctadecane
7	3,4-epoxy-2-methyloctadecane
8	4,5-epoxy-2-methyloctadecane
9	5,6-epoxy-2-methyloctadecane
10	6,7-epoxy-2-methyloctadecane
11	8,9-epoxy-2-methyloctadecane
12	9,10-epoxy-2-methyloctadecane
13	7,8-epoxy-3-methyloctadecane
14	7,8-epoxy-4-methyloctadecane
15	7,8-epoxy-5-methyloctadecane
16	7,8-epoxy-6-methyloctadecane
17	7,8-epoxy-7-methyloctadecane
18	7,8-epoxy-8-methyloctadecane
19	7,8-epoxy-9-methyloctadecane
20	7,8-epoxynonadecane
21	5,6-epoxy-3-ethylheptadecane
22	6,7-epoxy-5-ethylheptadecane
23	9,10-epoxy-5-ethylheptadecane
24	5,6-epoxy-2,2-dimethylheptadecane
25	6,7-epoxy-3,4-dimethylheptadecane
26	7,8-epoxy-5,5-dimethylheptadecane
27	8,9-epoxy-2,6-dimethylheptadecane
28	6,7-epoxy-4-methyloctadecane
29	6,7-epoxy-3-methyloctadecane
30	8,9-epoxynonadecane

Since epoxides are prepared readily from olefins with *m*-chloroperbenzoic acid, mass spectrometric procedures that determine epoxide position may be useful in determining double bond position at the nanogram level. Such data could supplement or replace ozonolysis procedures for the same determination.

EXPERIMENTAL PROCEDURES

As described by Sarmiento, et al. (6), the olefin precursors of the epoxides were synthesized by the Wittig reaction, purified by chromatography on a silver nitrate-silica gel column, and then epoxidized with *m*-chloroperbenzoic acid.

The compounds (Table I) were introduced into a Finnigan 1015 mass spectrometer via the batch inlet, and the spectra were recorded at 70 ev and 250 μa with 10 sec scans. The percent abundances are given vs the base peak as

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[1] ARS, USDA.

100%. No significant spectral differences were noted between *cis*- and *trans*-epoxides; the data reported are for the *cis*-isomers.

RESULTS AND DISCUSSION

vic-Dialkyl Epoxides

α-, β-, and γ-Cleavage: Each of the three cleavage or fission processes yields four possible fragments from $R{-}\underset{O}{CH{-}CH}{-}R'$, where R′ is the longer of the two alkyl groups. For example, α-cleavage yields R^+, R'^+, $R{-}\underset{O}{CH{-}CH^+}$, and $R'{-}\underset{O}{CH{-}CH^+}$, and each of these falls in the m/e series 43, 57, 71....

The mass spectra of the 27 disubstituted compounds indicate that the lower fragments of this series, namely m/e 43, 57, 71, 85, and 99, are unreliable for structure diagnosis in the higher mol wt compounds of this study. Concurrent C–C cleavage along the alkyl chains produces other C_nH_{2n+1} fragments that also fit into this mass series but are unrelated to the epoxide position. Therefore, intensities at these masses are high for all the compounds, regardless of epoxide position; with the compounds studied, the overall range of abundances for each mass is as follows: m/e 43 (42-100%), m/e 57 (39-100%), m/e 71 (19-100%), m/e 85 (10-51%), and m/e 99 (2-20%).

Fragments with the higher m/e values in this series (113, 127, 141....) are characteristic of the epoxide group position. α-Cleavage with loss of the larger alkyl group generates fragments of $R{-}\underset{O}{CH{-}CH^+}$ that have abundances of 4-20% in 26 of the 27 compounds. Similar cleavage of the smaller alkyl group gives $R'{-}\underset{O}{CH{-}CH^+}$ fragments of 1.3-16% abundance; for all but two of the compounds, this range narrows to 4-16%. Background intensities for the higher members of the series, m/e 113, 127, 141, ... (where no special structures exist) are much lower, ranging from 1.2-4.8% at m/e 113 and 0.7-3.0% at the higher masses (127, 141, etc.).

Plots of percent abundance vs m/e for the 57, 71, 85.... mass series (Fig. 1) show maxima corresponding to $R{-}\underset{O}{CH{-}CH^+}$ and $R'{-}\underset{O}{CH{-}CH^+}$ for α-cleavage. In 25 of the 27 compounds, the intensities of the two $C_nH_{2n-1}O$ fragments resulting from α-cleavage exceeded the intensities of other masses of the series and, thus, indicated the epoxide position along the chain. In the other two compounds, the intensity of only one of the two fragments was significantly greater than the background intensities.

The only other fragmentation that gives an abundance of ions above background in the m/e 113, 127, 141, etc. series results from cleavage that is both γ to the epoxide and α to a methyl (but not ethyl) or dimethyl branch, i.e.:

$$R\underset{O}{CHCH}CH_2CH_2{}^+\!\mid\!\underset{CH_3}{CH}{-}\ \text{or}\ R\underset{O}{CHCH}CH_2\underset{CH_3}{CH^+}\!\mid\!CH_2{-}.$$

In each of the compounds with this structure (14, 15, and 24-29), the $C_nH_{2n-1}O$ fragment was m/e 197, 211, 225, or 239, and its abundance ranged from 1.2-7.2% which is less than the abundances from the α-cleavage fragments. Typical maxima for the two O-containing α-cleavage fragments, as well as those from the combined γ-α-methyl cleavage, are shown in the plot of data from compound 29 in Figure 1.

γ-Cleavage (other than that also α to a methyl branch) and β-cleavage are not significant processes in the disubstituted epoxides analyzed. The $C_nH_{2n-1}O$ products from β- and γ-fragmentations, as well as the C_nH_{2n+1} ions from α-,β, and γ-cleavages were not sufficiently abundant in the m/e 113, 127, 141.... mass series for characterization.

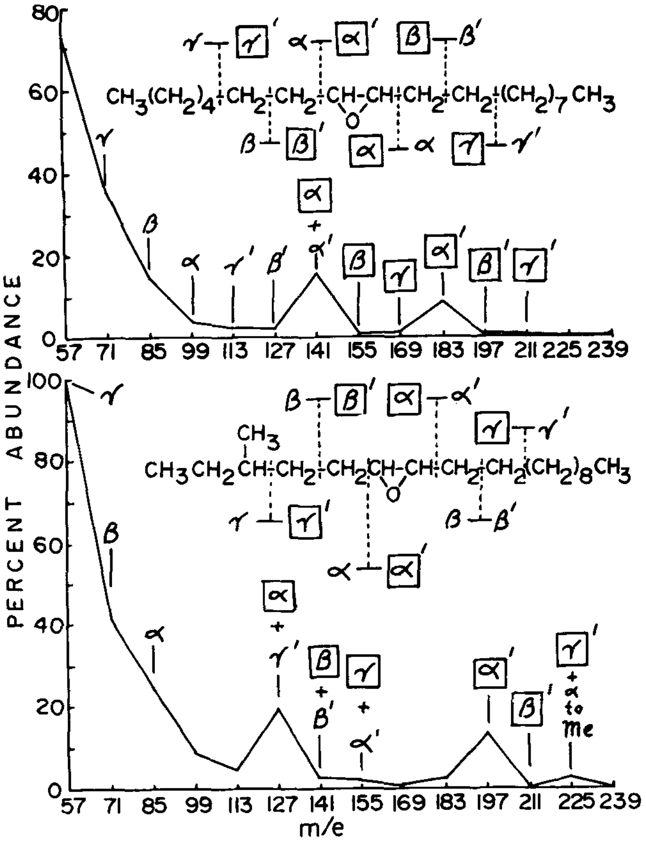
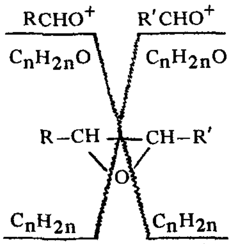


FIG. 1. Abundance of fragments from α-, β-, and γ-cleavages of 8,9-epoxynonadecane (top) and of 6,7-epoxy-3-methyloctadecane (bottom).

Transannular cleavage: As described by Budzikiewicz, et al. (4), transannular cleavage yields four possible products, plus an additional two when H-transfer is considered:



C_nH_{2n} → m/e 56, 70, 84, 98....

$C_nH_{2n}O$ → m/e 58, 72, 86, 100....

$C_nH_{2n+1}O$ (Htransfer)→m/e 59, 73, 87 ..

All compounds showed abundant fragments in both of the even mass series below m/e 98, and structure characterization is unreliable in this region. At m/e 98 and above, the abundances of fragments from the 27 disubstituted epoxides fall in the following ranges: R–CH, 1-23% (and 1-10% for 25 of the 27 compounds); RCHO, not detected (ND)-9%; R′CH, ND-2%; and R′CHO, ND-2%. The background intensities in both of these mass series, i.e. peaks not assignable to transannular cleavage, are as high as 14% but decrease with increasing mass. With this background and such relatively low abundances for the C_nH_{2n} and $C_nH_{2n}O$ fragments, only the RCH^+ (but not $R'CH^+$) ion is distinguishable above background in plots of abundance vs m/e for the two even mass series (plots A and B in Figure 2). The $C_nH_{2n}O$ products from McLafferty rearrangement were not detected.

In the series $C_nH_{2n+1}O$ from transannular cleavage plus H-transfer, the total range of abundances in the series m/e 101, 115, 129.... for $RCHOH^+$ is 0.5-9% and for $R'CHOH^+$ is ND to 1.3%. The background values at these masses are as high as 2% but are generally less than 1%. Only compounds

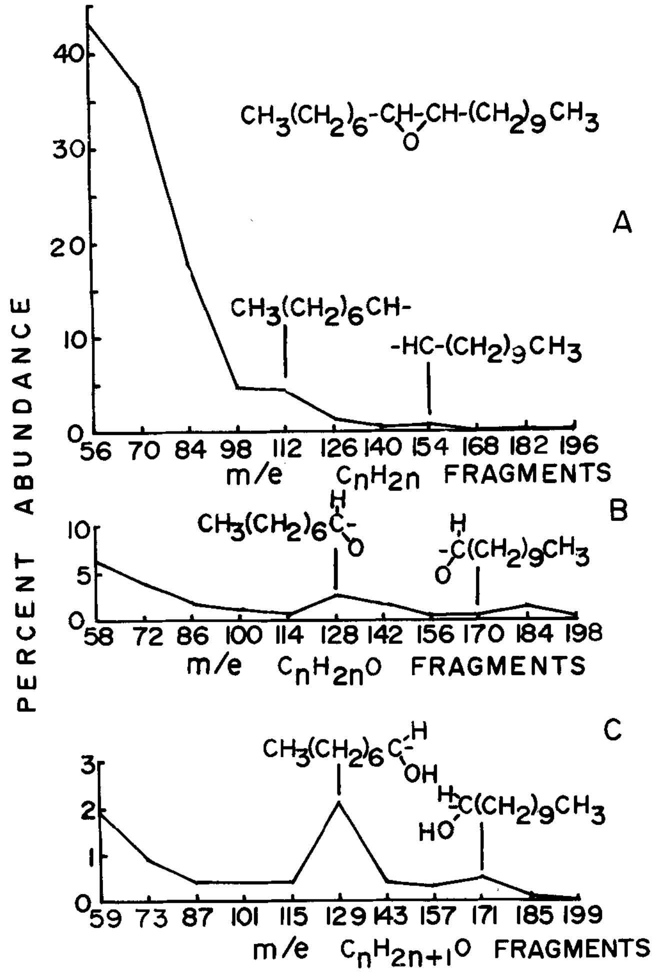


FIG. 2. Abundance of fragments from transannular cleavage of 8,9-epoxynonadecane: A. C_nH_{2n}, B. $C_nH_{2n}O$, and C. $C_nH_{2n+1}O$.

7 and 8 have $RCHOH^+$ fragments at the lower end of this m/e series, i.e. at m/e 59, 73, or 87, and these have the high abundances of 50 and 15%, respectively; the background at these masses is 6% or less. A plot of percent abundance vs m/e for this mass series (Fig. 2C) shows a maximum for $RCHOH^+$ and, thus, can provide evidence for the epoxide position. The abundance of $RCHOH^+$ at and above m/e 143 and of R'CHOH at all the masses is so low (ca. 1% or less) that structure identification from this fragmentation may not be certain.

Transannular cleavage with H-transfer is favored in compounds containing a methyl or ethyl branch α to the epoxide; the resulting abundances of $RCHOH^+$ and $R'CHOH^+$ are always at the high end of the quoted ranges and give significant maxima in the plots of percent abundance vs m/e.

Transannular cleavage plus water elimination: The most useful fragmentation pattern found for structure diagnosis is often the C_nH_{2n-2} series m/e 54, 68, 82.... Cleavage between the epoxide carbon atoms, plus elimination of water from $[\underset{\diagdown O}{R-CH}]^+$, could yield this fragment. Concurrent with this fragmentation is the production of similar C_nH_{2n-2} ions (n = 5 and 6 and to a lesser extent 4 and 7) from the alkyl side chains, but this is unrelated to the epoxide group position; therefore, the background is high, and the diagnostic value of fragments with m/e 54, 68, 82, and 96 is reduced. Nevertheless, when the mass of a C_nH_{2n-2} fragment is m/e 110 or higher, it is recognized readily as a maximum in the plot of percent abundance vs m/e for this mass series (Fig. 3). When maxima do occur in such plots, they clearly indicate the position of the epoxide group along the chain.

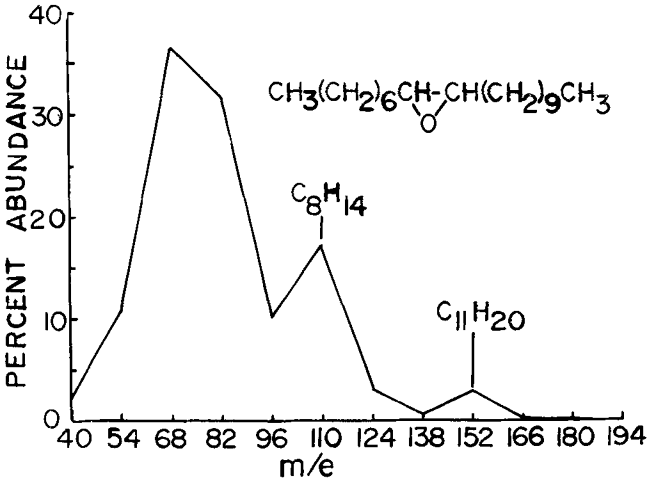


FIG. 3. Abundance of fragments from transannular cleavage, plus water elimination, of 8,9-epoxynonadecane.

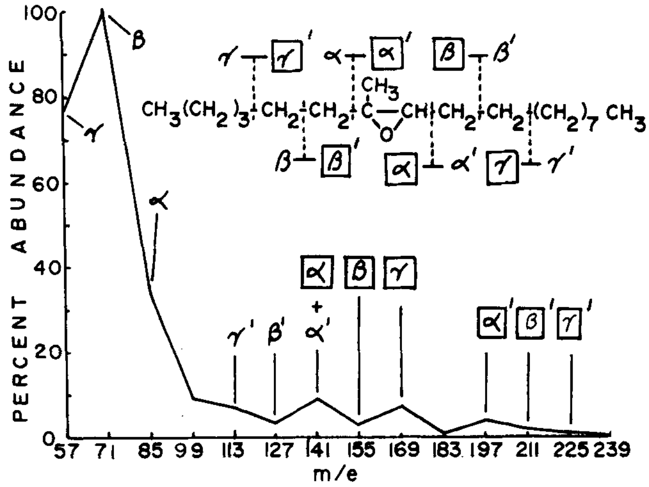


FIG. 4. Abundance of fragments from α-, β-, and γ-cleavages of 7,8-epoxy-7-methyloctadecane.

Other fragments: The abundance of the molecular ion (M^+) for the 24 disubstituted epoxides that do not contain a methyl or ethyl branch α to the epoxide ranges from ND-0.6%. The three compounds containing such a branch show M^+ abundances of 0.5-1.4%.

Two other mass series corresponding to C_nH_{2n-3} and C_nH_{2n-1} and $C_nH_{2n-3}O$ are present in all the spectra but are not useful for epoxide location.

Trialkyl Epoxides

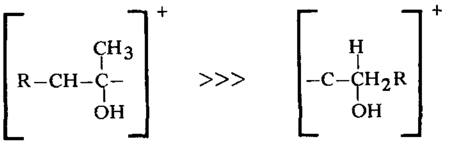
α, β, and γ-Cleavage: Of the compounds analyzed, there are only 3 trialkyl epoxides, namely numbers 6, 17, and 18. As with the disubstituted compounds, α-,β-, and γ-cleavage yield C_nH_{2n+1} and $C_nH_{2n-1}O$ fragments, all of which fall in the m/e series 43, 57, 71.... Masses of 99 and below are unreliable for epoxide location in these high mol wt compounds due to overlapping fragments from chain cleavage, as described previously.

Plots of abundance vs m/e show maxima for the $C_nH_{2n-1}O$ fragments of α-cleavage (Fig. 4), but the maxima tend to be lower for the trisubstituted than for the disubstituted compounds. In addition, γ-cleavage gives some fragments that are more distinctive than with the disubstituted epoxides. Unlike the disubstituted epoxides, these three compounds show abundant $C_nH_{2n}O$ fragments from cleavage α to the epoxy group, plus transfer of a proton. These fragments fall in the m/e series: 72, 86, 100.... which is the same series that contains the $RCHO^+$ and $R'CHO^+$ fragments from transannular cleavage. Figure 5B shows that these α-cleavage, plus H-transfer fragments, are recognized easily and quickly indicate the epoxide position in structure identification.

Both β- and γ-cleavages give more abundant fragments than observed with the disubstituted compounds.

γ-cleavage in the longer alkyl group gives an enhanced $C_nH_{2n-1}O$ fragment, as compared to similar cleavage in disubstituted compounds (m/e 169 in compounds 17 and 18 [Fig. 4]).

Transannular cleavage: As described for disubstituted epoxides, only the RCH^+ fragment of transannular cleavage (no proton transfer) has a sufficiently large intensity for recognition (Fig. 5A). The $R'CH^+$ and the 2 $C_nH_{2n}O$ fragments have low intensity (Fig. 5A and 5B). Although transannular cleavage with H-transfer gives two $C_nH_{2n+1}O$ products, the one containing the methyl substituent is much more abundant.



$$\left[\mathrm{R{-}CH{-}\overset{\displaystyle CH_3}{\underset{\displaystyle OH}{C}}{-}}\right]^+ >>> \left[\mathrm{{-}\overset{\displaystyle H}{C}{-}\underset{\displaystyle OH}{C}H_2R}\right]^+$$

Compounds 17 and 18, which differ only in the position of the methyl substituent, readily show this cleavage preference (Fig. 5C and 5D). In disubstituted epoxides, the size of the R group was the major factor in determining the relative abundance of the two products from transannular cleavage plus H-transfer.

Other fragments: The molecular ion for the trisubstituted compounds ranged from ND-0.6%. As with the disubstituted epoxides, spectra of these compounds showed abundant fragments of C_nH_{2n-3} and C_nH_{2n-1} and $C_nH_{2n-3}O$ which were not useful for structure identification.

As a final comment, we note that, though characterization of an unidentified compound made by examining the individual m/e series can be very reliable, some caution in interpretation is necessary, because of the possibility of unrecognized isobaric patterns in low resolution spectra (4).

A method describing the location of epoxide position of aliphatic epoxides from their chemical ionization mass spectra has recently appeared (7).

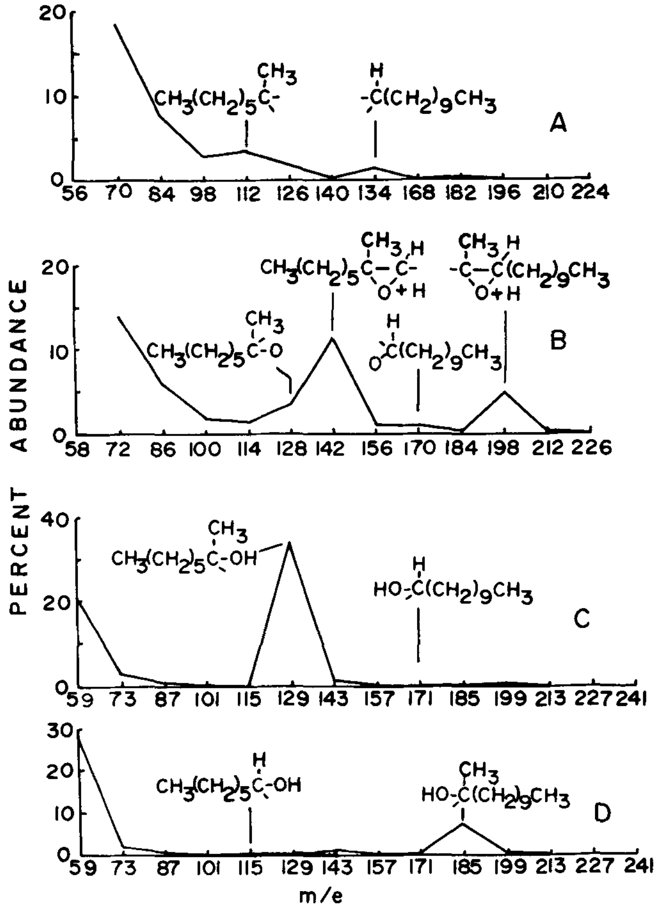


FIG. 5. Abundance of fragments from transannular cleavage of 7,8-epoxy-7-methyloctadecane (A, B, and C) and 7,8-epoxy-8-methyloctadecane (D). In addition, α-cleavage, plus H-transfer (142 and 198 ions), is shown in B.

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