The Analysis of 1,2-Epoxyalkanes by Gas Liquid Chromatography[1]

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Abstract

Terminal epoxides react quantitatively with methanol in the presence of boron trifluoride to give both primary and secondary hydroxy methyl ethers. These derivatives are useful in the analysis of terminal epoxide mixtures by gas liquid chromatography. This procedure is compared with the conventional method and with a procedure in which the 1,2-epoxyalkanes are reduced to the corresponding secondary alcohols with $LiAlH_4$. A statistical analysis of experimental data obtained from known mixtures of long chain epoxides is described. Results of this analysis demonstrate the improved accuracy and precision of the method as compared to the other methods investigated. $LiAlH_4$ reduction is the preferred method of analysis for the more reactive epoxides as well as for the cyclic epoxides. This procedure is particularly useful in the analysis of epoxides containing a tertiary carbon atom. The application of this technique to other epoxides is expected to improve their analysis, but further work is necessary.

Introduction

Since Nicolet and Poulter (1) first reported the quantitative determination of epoxide groups in 9,10-epoxy-stearic acid using a hydrohalogenation procedure, numerous chemical and instrumental methods for assaying the oxirane function have appeared in the literature. The majority of these methods have been chemical in nature (2). The instrumental methods for the most part have been limted to infrared spectroscopy. Until recently methods utilizing gas liquid chromatography (GLC) have been noticeably absent from the literature. Fiorti et al. (3) have applied GLC to the analysis of epoxyglycerides as their 1,3-dioxolane derivatives, but conversion is not quantitative.

Terminal epoxides can be separated directly by GLC, but thermal rearrangement of the sample during passage through the column limits the usefulness of this technique (3) and makes quantitative recovery of components difficult. The use of an all-glass system with on-column injection minimizes the problems associated with heat lability but does not allow adequate separation of the epoxides from the corresponding unreacted olefins or from impurities present in the sample. In addition, the increase in peak width with increasing chain length and the large variation of relative response factors with chain length preclude the use of such a method for quantitative analysis.

The reaction of 1,2-epoxyalkanes with alcohols in the presence of a Lewis acid catalyst such as boron trifluoride to give the isomeric hydroxy alkyl ethers is well known (4). The application of this reaction to the preparation of suitable derivatives which are thermally stable and which allow adequate separation of the different epoxides from the corresponding olefins is discussed. Quantitative analysis is facilitated by the linear relationship of the relative response factors as a function of chain length for a given series of long chain terminal epoxides. The above procedure also is compared to the $LiAlH_4$ reduction of 1,2-epoxyalkanes followed by GLC analysis. This latter technique is more time consuming and more complicated than the boron trifluoride procedure. However, it is preferred for certain systems and will be discussed in more detail in a subsequent paper.

Experimental Procedures

Boron Trifluoride in Methyl Alcohol

One half milliliter of sample was dissolved in an equal amount of isooctane in a 5 ml vial. Then 1 ml of 10% cold boron trifluoride in methanol was added dropwise. The mixture was shaken until the solution became clear. The reaction was terminated by shaking the mixture for 1 min with an excess of saturated aqueous NaCl. The vial was allowed to stand at room temperature until two distinct layers formed. The top layer was sampled directly for GLC analysis.

Lithium Aluminum Hydride Reduction

A slurry of $LiAlH_4$ in diethyl ether was prepared at room temperature. A solution of the sample in anhydrous ether was added dropwise to the reducing agent and the mixture stirred for at least 2 min. Water was added, followed by aqueous NaOH (15%) according to the procedure of Micović and Mihailović (5), and the slurry stirred until hydrolysis of the excess $LiAlH_4$ was complete. More water was added (5) and the mixture stirred until a white crystalline precipitate formed. The precipitate was filtered and washed with ether. The filtrate was dried with sodium sulfate, concentrated under nitrogen and sampled for GLC analysis.

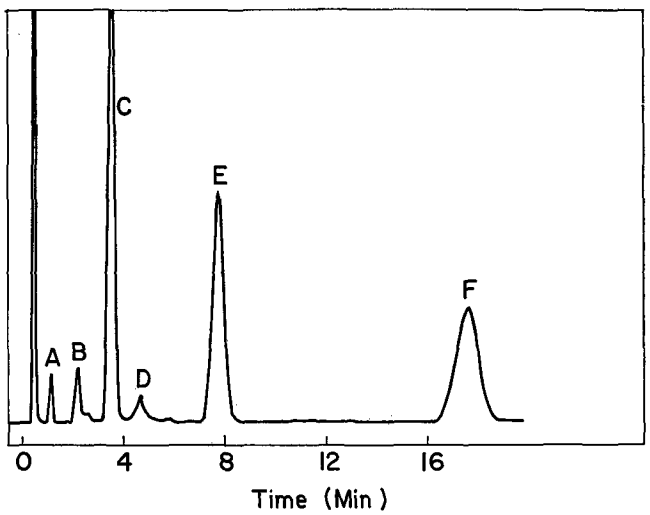

FIG. 1. Chromatogram of a mixture of 1,2-epoxyalkanes together with the corresponding α-olefins: (A) 1-dodecene, (B) 1-tetradecene, (C) 1,2-epoxydodecane, (D) 1-hexadecene, (E) 1,2-epoxytetradecane and (F) 1,2-epoxyhexadecane.

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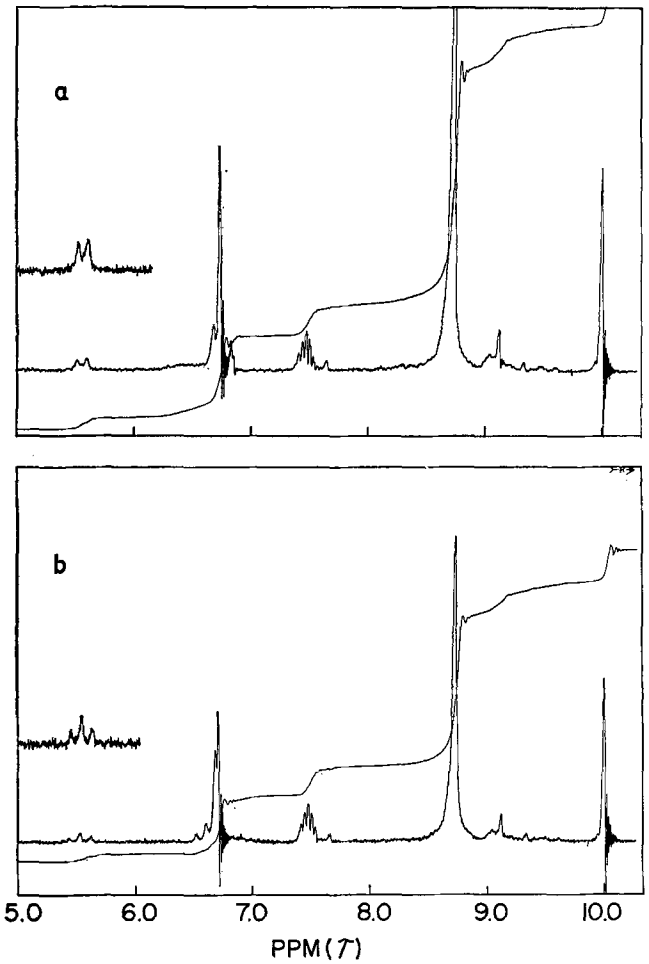


FIG. 2. Proton resonance spectra of the hydroxy methyl ether derivatives of 1,2-epoxydodecane: (a) 2-hydroxy-1-methoxydodecane and (b) 1-hydroxy-2-methoxydodecane.

Equipment

All analyses were carried out on a Hewlett Packard Model 5754 B gas chromatograph equipped with dual flame ionization detectors. A 10 ft × ⅛ in. o.d. stainless steel column packed with 5% FFAP on 80/100 mesh Gas Chrom Q was used in all analyses involving both the hydroxy methyl ether derivatives and the secondary alcohol derivatives. This column was programmed from 100 C to 250 C at 6 C/minute with a flow rate of 20 ml of helium per minute. All analyses of terminal epoxides on the "as is" basis were carried out on a 10 ft × 1.5 mm i.d. glass column packed with 5% OV-22 on 80/100 mesh Chromasorb G. It was operated isothermally at 150 C with a helium flow rate of 20 ml/min. On-column injection techniques were used. The areas under all the GLC curves were computed with a Hewlett Packard Model 3370A digital integrator.

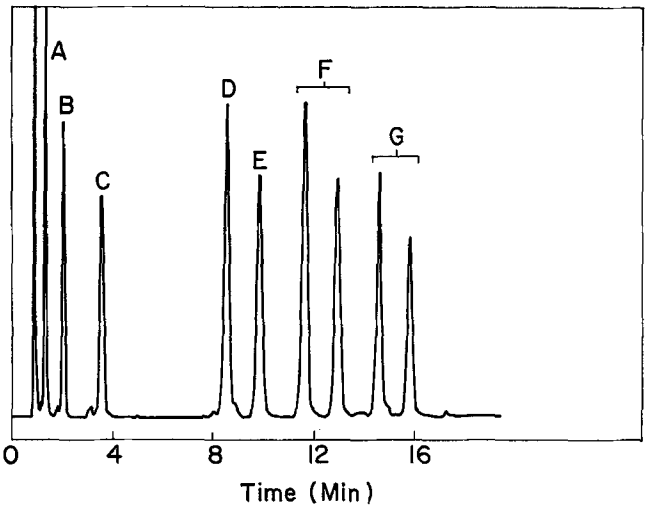


FIG. 3. Chromatogram of the hydroxy methyl ether derivatives of a mixture of 1,2-epoxyalkanes along with the corresponding α-olefins: (A) 1-dodecene, (B) 1-tetradecene, (C) 1-hexadecene, (D) 2-hydroxy-1-methoxydodecane, (E) 1-hydroxy-2-methoxydodecane, (F) 2-hydroxy-1-methoxytetradecane and 1-hydroxy-2-methoxytetradecane and (G) 2-hydroxy-1-methoxyhexadecane and 1-hydroxy-2-methoxyhexadecane.

NMR spectra were obtained with a Varian A-60A spectrometer operating at a frequency of 60 MHz. All samples were examined in deuterated dimethyl sulfoxide containing the sodium salt of 3-(trimethylsilyl)-propanesulfonic acid as the internal standard.

Discussion

Mixtures of 1,2-epoxyalkanes and the corresponding olefins from which they are prepared together with the customary impurities offer a most difficult problem in any direct analysis by GLC. Figure 1 represents the curve obtained for a known mixture of 1,2-epoxyalkanes with chain lengths of 12 through 16 together with the corresponding α-olefins. The concentrations of the α-olefins are higher than those expected in commercial samples of terminal epoxides, and their separation from impurities is marginal at best. The peak width increases with increasing chain length and the relative response factors of the 1,2-epoxyalkanes are a nonlinear function of chain length.

Methyl alcohol reacts readily with terminal epoxides in the presence of boron trifluoride, a Lewis acid catalyst, to give two isomeric hydroxy methyl ethers. Using a C_{12} epoxide, both isomers were isolated by preparative GLC and examined by NMR spectroscopy. Figure 2a and 2b represent the NMR spectra of the secondary alcohol (primary ether) which emerges from the column first and the primary alcohol (secondary ether), respectively. The characteristic spin-spin splitting (6) of the secondary alcohol, a

TABLE I

Analysis of Known Mixtures of Olefin Oxides[a]

Mixture	Component	Known Wt. %	Experimental Wt. %										Standard deviation
			1	2	3	4	5	6	7	8	9	10	Mean	
1	C_{12}	22.8	22.1	22.8	22.2	22.7	22.5	22.3	22.9	21.9	22.6	22.5	22.5	0.321
	C_{14}	34.5	34.8	34.2	35.7	34.5	34.2	35.2	35.0	35.7	35.9	35.0	35.0	0.614
	C_{16}	42.7	43.1	43.0	42.1	42.8	43.3	42.5	42.1	42.4	41.5	42.5	42.5	0.544
2	C_{12}	24.5	24.2	24.2	24.4	24.2	24.5	24.0	23.7	24.1	24.3	24.2	24.2	0.220
	C_{14}	51.6	52.2	51.8	52.4	51.8	52.0	52.4	51.6	51.9	52.1	52.4	52.1	0.288
	C_{16}	23.9	23.6	24.0	23.2	24.0	23.8	23.9	23.4	23.8	24.1	23.7	23.7	0.284

[a] Column, 10 ft × ⅛ in. FFAP on Gas Chrom Q (5% by wt.). Temperature, programmed from 100 C to 260 C at 6 C/min. Carrier Gas, Helium, 20 ml/min. Sample size, 0.1 μl.

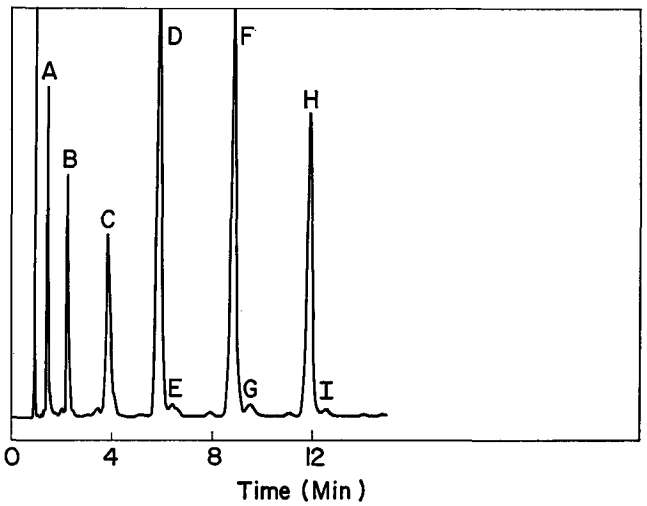
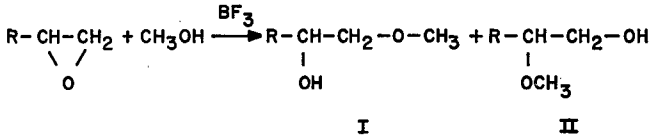


FIG. 4. Chromatogram of the $LiAlH_4$ reduction products of a mixture of 1,2-epoxyalkanes together with the corresponding α-olefins: (A) 1-dodecene, (B) 1-tetradecene, (C) 1-hexadecene, (D) 2-hydroxydodecane, (E) 1-hydroxydodecane, (F) 2-hydroxytetradecane, (G) 1-hydroxytetradecane, (H) 2-hydroxyhexadecane and (I) 1-hydroxyhexadecane.

doublet, and of the primary alcohol, a triplet, occurs at τ 5.57 and τ 5.55, respectively. The expected chemical shift of the methoxy group occurs at τ 6.75 for both isomers. Equation 1 illustrates the reaction of methanol with pure 1,2-epoxyalkanes containing 12,



R	I	II
C_{10}	58%	42%
C_{12}	59%	41%
C_{14}	60%	40%

14 and 16 carbon atoms. The product distribution of the two isomers remains constant as the chain length increases. The mechanism of this reaction reportedly (7) proceeds through protonation of the ring oxygen, followed by ring opening in either direction to give relatively equal yields of both products. Lebedev et al. (7), however, used 1,2-epoxypropane as their model compound. In the case of long chain terminal epoxides attack at the 1 position seems to be favored, possibly due to steric effects, resulting in a higher yield (60%) of the secondary alcohol (primary ether).

Figure 3 shows the separation of the hydroxy methyl ether derivatives of a known mixture similar in composition to that represented in Figure 1. The α-olefins are well separated from the isomeric derivatives of the corresponding epoxides. In addition, the separation between isomers of any single epoxide and between both isomers of different epoxides is more than adequate for accurate quantitative analysis. The chromatographic peaks are all sharp and well defined. The relative response factors of the hydroxy methyl ether derivatives are a linear function of chain length.

The results of analyses of two known mixtures are shown in Table I. In both mixtures the experimentally determined weight percentages are in good agreement with the known sample composition. The 1,2-epoxyalkanes were prepared from α-olefins of known purity obtained from the Chevron Co. The oxirane

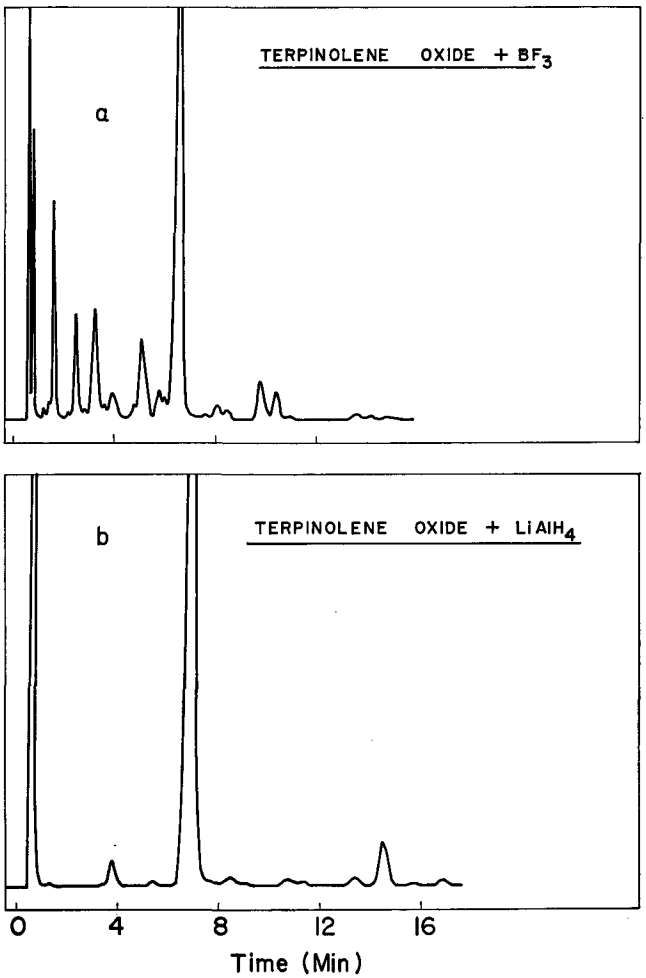


FIG. 5. GLC separation of the reaction products of terpinolene oxide with (a) BF_3-methanol and (b) $LiAlH_4$.

content was checked according to the classical chemical procedure (8). A statistical analysis of only five replicate determinations is obviously of limited value, but the standard deviation for each set of data is included in Table I.

$LiAlH_4$ reacts with 1,2-epoxyalkanes to yield the secondary alcohol as the predominant product (> 95%) and a small amount (<5%) of primary alcohol as the by-product. The reaction scheme is shown in Equation 2. The reactive species is reportedly (9) a series of complex aluminohydride ions, $AlH_{4-n}R_n^-$, which act as carriers for the hydride ion.

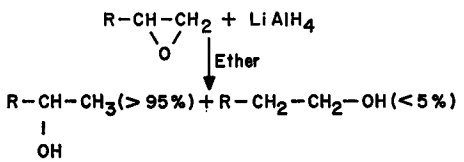


Figure 4 shows the separation of the reduction products of a known mixture of terminal epoxides with chain lengths of 12, 14 and 16 carbon atoms along with the corresponding α-olefins. Although separation of the α-olefins from the reduction products is adequate, the resolution of the primary and secondary alcohols is only marginal. This limitation, making accurate integration more difficult, together with the substantial time required to prepare the derivatives, points to the boron trifluoride procedure as the preferred method for such an analysis.

$LiAlH_4$ reduction, however, is a convenient method for the analysis of the more reactive epoxides such

as isobutylene oxide and styrene oxide. Additionally, the boron trifluoride procedure is not applicable to epoxides whose derivatives are soluble in water as is the case with isobutylene oxide. The $LiAlH_4$ procedure is also more useful in the analysis of cyclic epoxides, such as 1,2-epoxycyclohexane, 1,2-epoxycyclooctane and 1,2-epoxycyclododecane. Only one product is formed with the cylic epoxides.

Tertiary epoxides offer a much more difficult analytical problem since their properties differ from those of other epoxides. The usual hydrohalogenation procedures give poor results with the tertiary epoxides. Durbetaki (11) has reported a procedure based on isomerization of the epoxide to the corresponding aldehyde, followed by gravimetric determination of the 2,4-dinitrophenylhydrazone derivative. This procedure, however, is both tedious and time consuming. Also, the reaction of methanol with the oxides of α-pinene, limonene and terpinolene in the presence of boron trifluoride gives a mixture of products which are not amenable to analysis by GLC. In contrast, $LiAlH_4$ reduction of epoxides containing a tertiary carbon atom, followed by GLC, affords a relatively simple and rapid method of analysis. Figure 5a and 5b represent the curves obtained for terpinolene oxide using methanol-boron trifluoride and $LiAlH_4$, respectively. The advantages of the latter procedure over the former are obvious. A more detailed examination of the quantitative aspects of this procedure will be presented in a subsequent paper.

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