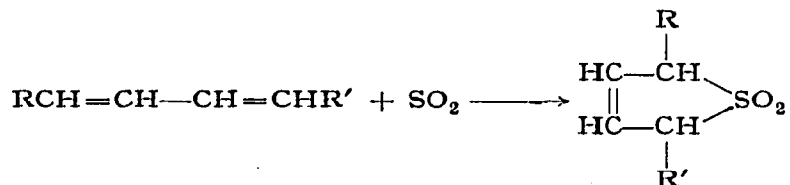
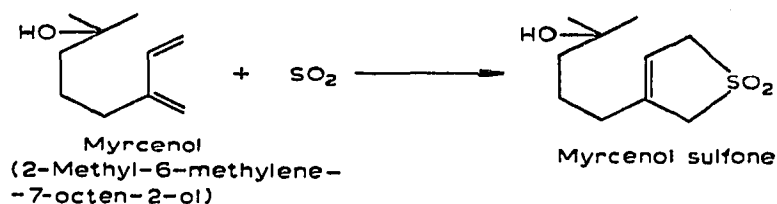
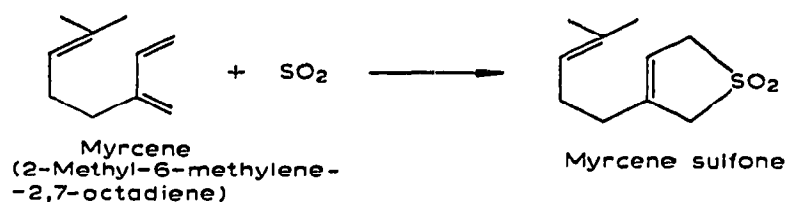


Quantitative determination of conjugated diene sulfone addition products by a combination of gas-liquid chromatography and infrared analyses*

The addition of SO_2 to a conjugated dienic system results in the formation of a cyclic sulfone¹:



A procedure was required for the analysis of these types of sulfones and myrcene sulfone and myrcenol sulfone were selected as the compounds for detailed study.



A "wet" chemical method based on total sulfur content² gave inconsistent results due to the presence of sulfur dioxide and organically-bound sulfur in compounds other than myrcene sulfone. An infrared procedure, utilizing the sulfone absorption band at 7.6μ (1316 cm^{-1}), was not applicable for the same reasons.

A gas-liquid chromatographic (GLC) method based on the elution of myrcene sulfone also proved unsuccessful. Due to the thermal instability of the compound, it was necessary to bypass the injector and introduce the sample directly onto the column. Since the column temperature had to be maintained sufficiently low to prevent decomposition of the sample (*ca.* 70°), extremely long elution times (2 h) using lightly loaded (2 %) columns resulted and the reproducibility was unsatisfactory.

The method finally employed to give accurate and reproducible analyses was based on a combination of an infrared measurement at 6.25μ (1600 cm^{-1}) of unreacted conjugated diene and the complete thermal decomposition of the sulfone to myrcene (retro-Diels-Alder reaction) in the gas-liquid chromatograph.

* This paper was presented at the second Middle Atlantic American Chemical Society Meeting in New York City, February 6th, 1967.

*Experimental**I. Infrared determination of myrcene in myrcene sulfone**A. Conditions*

Instrument: Beckman Model IR-4
 Cell path: 0.018 mm
 Prism: NaCl
 Speed: 0.5 μ /min
 Scale: 2 in./ μ
 Gain: 2.5
 Period: 2
 Ordinate scale: 0.100

B. Procedure

Three known weight percent samples of myrcene in nonane were prepared to cover the concentration range expected in the experimental samples. Using an 0.018 mm cell, the known mixtures were scanned from 5.5 μ (1818 cm^{-1}) to 7.0 μ (1429 cm^{-1}). The absorbance at 6.25 μ (1600 cm^{-1}) was plotted against the weight percent and linear results were obtained. To calculate the percentage of myrcene, the absorbance at 6.25 μ (1600 cm^{-1}) was measured and the weight percent myrcene read directly from the graph.

C. Analytical data

For analytical data see Table I and Fig. 1.

TABLE I
 INFRARED CALIBRATION CURVE DATA

	<i>Known mixtures</i>		
	<i>Std. I</i>	<i>Std. II</i>	<i>Std. III</i>
Weight myrcene ^a (corrected for purity) (g)	0.2438	0.4857	0.7400
Weight nonane (diluent) (g)	0.7490	0.5120	0.2552
Total weight (g)	0.9928	0.9977	0.9952
Weight percent myrcene	24.6	48.6	74.4
Absorbance (arbitrary units)	0.211	0.404	0.610

^a Myrcene—95% pure by GLC, area normalization and ultraviolet absorption.

II. A GLC internal standard method for myrcene sulfone using ethyl octanoate as the internal standard

The GLC method was based on the quantitative decomposition of myrcene sulfone to myrcene and SO_2 . From Table II it is seen that a minimum temperature of 350° is required to completely decompose the sample.

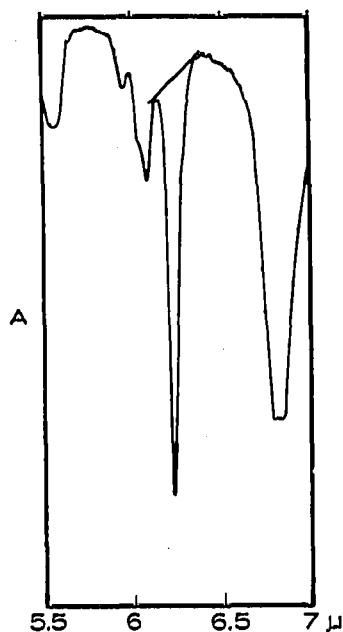


Fig. 1. Infrared spectrum of myrcene (5.5 μ to 7.0 μ).

TABLE II

EFFECT OF INJECTOR TEMPERATURE ON THE DECOMPOSITION OF MYRCENE SULFONE

Injector temperature (°C)	% myrcene sulfone
160	66.2
200	72.4
250	83.0
350	93.5
400	93.0

A. Conditions

Instrument: F & M Model 720

Column: 20 ft. (1/4 in.) copper tubing containing 5 % Carbowax 20 M on 60/80 mesh Chromosorb W* (silicone treated)

Column temperature: 120°

Helium inlet pressure: 40 p.s.i.

Flow rate: 200 ml/min

Chart speed: 60 in./h

Sample size: 1 μ l

Sensitivity: X8

Injection temperature: 400°

Elution time: 10 min

* Chromosorb (tradename), Johns Manville.

B. Procedure

Three known mixtures of myrcene* and ethyl octanoate** (internal standard) were prepared to cover the concentration range expected in the samples submitted for analysis.

The weight ratio of myrcene/ethyl octanoate was plotted against the average of the area ratios (myrcene/ethyl octanoate) obtained from the chromatogram. Several runs were made on each known mixture and linear results were obtained over the concentration range examined.

The samples under investigation were prepared by weighing a 1:1 mixture of the sample and ethyl octanoate. After the chromatograms were recorded, the area ratios (myrcene/ethyl octanoate) were calculated and the weight ratio obtained from the graph. To calculate the percentage of myrcene sulfone, the following equation was used:

$$\% \text{ myrcene sulfone} = \left(\frac{\text{wt. ratio} \times \text{wt. ethyl octanoate} \times 100}{\text{sample weight}} - \% \text{ free myrcene}^{***} \right) 1.47^{\S}$$

C. Analytical data

For analytical data on myrcene and myrcene sulfone see Table III and Fig. 2. For analytical data on myrcenol and myrcenol sulfone see Table IV and Fig. 2.

For qualitative analysis see Table V.

TABLE III
GLC CALIBRATION CURVE FOR MYRCENE SULFONE USING MYRCENE

	Known mixtures		
	Std. I	Std. II	Std. III
Weight myrcene ^a (g)	0.2913	0.2883	0.6465
Weight ethyl octanoate (g)	0.6758	1.5157	0.7172
Weight ratio $\left(\frac{\text{wt. myrcene}}{\text{wt. ethyl octanoate}} \right)$	0.431	0.190	0.901
Area ratio $\left(\frac{\text{area myrcene}}{\text{area ethyl octanoate}} \right)$	0.439	0.183	0.927
Average area ratio	0.427	0.183	0.913
	0.431	0.182	0.926

^a Corrected for purity.

Discussion

The following series of experiments were performed to validate the assumption that quantitative decomposition of the sulfone occurred in the gas-liquid chromatograph.

* See footnote to Table I.

** Ethyl octanoate, Eastman Organic Chemicals; no observable impurities by GLC.

*** The percentage of unreacted myrcene present in myrcene sulfone is determined by the infrared procedure described in Section IB.

§ The factor 1.47 is a correction for the molecular weight differences between myrcene sulfone and myrcene.

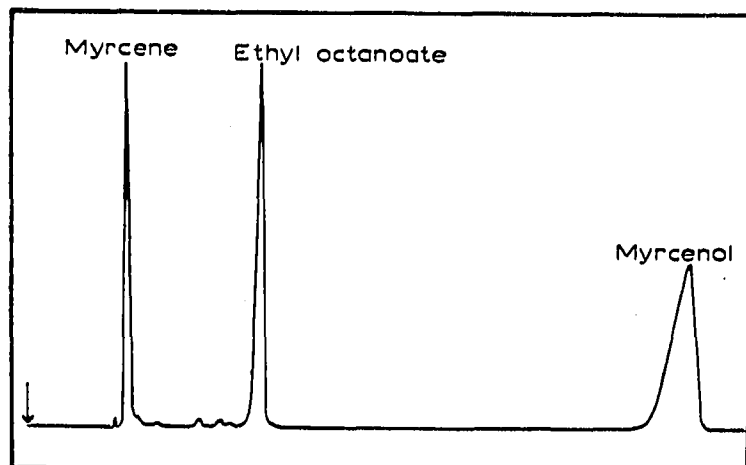


Fig. 2. GLC chromatogram of a mixture of myrcene and myrcenol containing ethyl octanoate as internal standard.

TABLE IV
GLC CALIBRATION CURVE FOR MYRCENOL SULFONE USING MYRCENOL

	<i>Known mixtures</i>		
	<i>Std. I</i>	<i>Std. II</i>	<i>Std. III</i>
Weight myrcenol ^a	0.2990	0.2143	0.3060
Weight ethyl octanoate (g)	0.5393	0.6731	0.3395
Weight ratio $\left(\frac{\text{wt. myrcenol}}{\text{wt. ethyl octanoate}}\right)$	0.554	0.318	0.901
Area ratio $\left(\frac{\text{area myrcenol}}{\text{area ethyl octanoate}}\right)$	0.453	0.283	0.734
Average area ratio	0.462	0.284	0.737
	0.460	0.282	0.735

^a Corrected for purity.

TABLE V
RELATIVE RETENTION TIME OF MYRCENE AND MYRCENOL TO ETHYL OCTANOATE

Myrcene	0.35
Ethyl octanoate	1.00
Myrcenol	2.00

A crude sample of myrcene sulfone was molecularly distilled and the fractions from this distillation were analyzed by the above-described method. Two of these fractions were submitted for NMR analyses and sulfur content. The NMR results obtained were as follows:

The signals of the NMR spectrum were given the assignments listed in Table VI.

Spectra were measured in CCl_4 solution on a Varian A-60 spectrometer. Chemical shifts are reported in p.p.m. relative to tetramethyl silane (internal standard).

TABLE VI
NMR ASSIGNMENTS FOR MYRCENE SULFONE

	<i>Chemical shift (p.p.m.)</i>
$\begin{array}{c} \\ \text{HC} - \text{C} - \text{S} - \\ \quad \end{array}$	5.68
$\begin{array}{c} > \text{C} = \text{CH} \\ \end{array}$	5.10
$\begin{array}{c} \text{=C} - \text{CH}_2 - \text{S} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{O} \end{array} \end{array}$	3.68
$\begin{array}{c} \text{=C} - \text{CH}_2 - \end{array}$	2.20
$\begin{array}{c} \text{H}_3\text{C} \\ \text{H}_3\text{C} \end{array} \text{C} =$	1.65

For quantitative measurements, the signal at 3.68 p.p.m. (protons of the two methylene groups alpha to the sulfone function) was assigned a value of four protons. All other integral values were then calculated based on the four-proton assignment, by simply setting up ratios of proton count to integral value. The deviation in calculated proton count from the theoretical count for myrcene sulfone was ascribed to impurity. The signal at 3.68 p.p.m. must be considered specific for the sulfone structure in the system under consideration; no terpene hydrocarbon moiety would give this chemical shift. The integration values used were the averages of at least five separate determinations and were measured by means of a Hewlett-Packard digital voltmeter.

Table VII summarizes the good agreement among GLC, NMR and sulfur determinations.

TABLE VII
COMPARISON AMONG GLC, NMR, AND SULFUR ANALYSES

<i>Fraction</i>	<i>GLC (%)</i>	<i>NMR (%)</i>	<i>Sulfur (%)</i>
5	94.8	94.0	95.0
9	97.0	96.1	98.0

III. A GLC method for myrcene sulfone (myrcene sulfone rather than myrcene used for known mixtures)

A. Conditions

Same as conditions described in Section IIB.

B. Procedure

Same as procedure described in Section IIB, except myrcene sulfone was used.

To calculate the percentage of myrcene sulfone, the following equation was used:

$$\% \text{ myrcene sulfone} = \frac{\text{wt. ratio} \times \text{wt. ethyl octanoate} \times 100}{\text{sample weight}}$$

C. Analytical data

For analytical data see Table VIII.

TABLE VIII
GLC CALIBRATION CURVE FOR MYRCENE SULFONE

	<i>Known mixtures</i>		
	<i>Std. I</i>	<i>Std. II</i>	<i>Std. III</i>
Weight myrcene sulfone (g)	0.1163	0.5034	0.3362
Weight ethyl octanoate (g)	0.2585	0.7009	1.7506
Weight ratio ($\frac{\text{weight myrcene sulfone}}{\text{weight ethyl octanoate}}$)	0.450	0.718	0.192
Area ratio ($\frac{\text{area myrcene sulfone}}{\text{area ethyl octanoate}}$)	0.263	0.419	0.107
Average area ratio	0.261	0.418	0.116
	0.265	0.412	0.112

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Received May 2nd, 1967