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SEPARATION OF PAIRS OF *cis*- AND *trans*-ISOMERS OF UNSATURATED SULPHUR COMPOUNDS BY GAS CHROMATOGRAPHY ON GRAPHITIZED CARBON BLACK

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SUMMARY

The conditions for the quantitative gas chromatographic analysis have been found for mixtures of *cis*- and *trans*-isomers of 1,2-diethyldithioethene, 1-ethoxy-2-(ethylthio)ethene, 1,2-diphenyldithioethene, 1-phenylsulphonyl-2-(phenylthio)ethene, ethyl ω-styryl sulphide and ethyl ω-styryl sulphone.

The preparative isolation of the *cis*- and *trans*-isomers of 1-ethoxy-2-ethylthioethenes has been performed.

INTRODUCTION

There are a number of publications on the gas–liquid chromatography (GLC) of sulphur compounds which are concerned mostly with the separation of saturated products[1–4]. The separation of substituted aromatic sulphur-containing acids[5,6] and the GLC of thiophene derivatives and related heterocyclic compounds[7,8] have been described.

The GLC of α,β-unsaturated sulphur compounds has not previously been studied in sufficient detail. There are only a few publications on the gas chromatographic (GC) separation of such compounds and most have dealt mainly with synthetic aspects[9–14]. The analytical- and preparative-scale separation of the *cis*- and *trans*-isomers of 1-ethoxy-2-(ethylthio)ethene has been reported[12], satisfactory separations of isomers being achieved with columns containing various packings. A column containing phthalate on acid-washed hexamethyldisilazane-treated Chromosorb W (60–80 mesh) was considered satisfactory. The retention times of the *cis*- and *trans*-isomers were reported to be 24 and 19 min, respectively, and the suitability of the column for the analysis was proved by the absence of additional peaks during injection of pure *cis*- and *trans*-isomers, isolated by means of preparative-scale GC.

The separation of stereoisomeric diphenyldithioethenes has also been described[10,11]. Schöllkopf *et al.*[10] analyzed *cis*- and *trans*-isomers of diphenyldithioethene on a column of Porapak Q (Perkin-Elmer, Norwalk, Conn., U.S.A.). There was no proof that thermal isomerization did not occur in the column used, and the correspondence between the ratio of the isomers as determined and the actual values was not adequately demonstrated. Ohno *et al.*[11] reported the analysis of *cis* and *trans* isomers on a column of the polysiloxane XE-60 at 200°. However, no information on the solid support, column dimensions or quantitative results obtained was provided.

Earlier, a quantitative determination of the *cis* and *trans* isomers of 1-ethylsulphonyl-2-alkylthioethenes ($C_2H_5SO_2CH{=}CHSC_nH_{2n+1}$; $n = 1$–12) was reported[15].

The quantitative GC determination of the *cis* and *trans* isomers of the following compounds is described in this paper: 1,2-diethyldithioethene ($C_2H_5SHC{=}CHSC_2H_5$), 1-ethoxy-2-(ethylthio)ethene ($C_2H_5OCH{=}CHSC_2H_5$), 1,2-diphenyldithioethene ($C_6H_5SCH{=}CHSC_6H_5$), 1-phenylsulphonyl-2-(phenylthio)ethene ($C_6H_5SO_2CH{=}CHSC_6H_5$), ethyl ω-styryl sulphide ($C_6H_5CH{=}CHSC_2H_5$) and ethyl ω-styryl sulphone ($C_6H_5CH{=}CHSO_2C_2H_5$). The adequacy of the analysis for each pair of isomers was checked by independent methods. Quantitative evaluation of the ratios of isomers was carried out by means of internal normalization. The internal standard method was also used.

EXPERIMENTAL

All measurements were carried out with an LCM-7 A chromatograph equipped with a flame ionization detector. Pure nitrogen was used as the carrier gas. Preparative-scale separation was carried out with an LCP-5 I instrument using argon as the carrier gas. The evaporators and columns of the analytical- and preparative-scale chromatographs were made of stainless steel. The internal diameters of the columns were 4 and 30 mm, respectively.

In some experiments, the fluorinated siloxane polymer SKTFT-50 was used as the liquid phase. In order to remove low-molecular-weight impurities, the polymer was dissolved in chloroform and precipitated by addition of 85% ethanol. The precipitated polymer was rinsed twice with 85% ethanol and dried thoroughly for 1 week in a vacuum desiccator.

Thin-layer chromatography of the compounds tested was carried out on neutral aluminium oxide of Brockman activity II. Nuclear magnetic resonance (NMR) spectra were obtained with a Varian Da160 instrument.

RESULTS

1,2-Diethyldithioethene

cis-1,2-Diethyldithioethene was prepared from 1,2-dichloroethene according to Kusa and McCombie[16]. It was a slightly yellowish liquid, b.p. 109°/15 mm (ref. 17). The *trans*-isomer was obtained by means of UV irradiation of the *cis*-isomer and was isolated from the reaction mixture using thin-layer chromatography in benzene–*n*-hexane (1 :7).

The analysis of the *cis* and *trans* isomers of 1,2-diethyldithioethene was carried out using a 3-m long column packed with Chromosorb W (80–100 mesh) and 10% LAC-IR-296 at 190°. A typical chromatogram is shown in Fig. 1. The column efficiency achieved was 3000 theoretical plates.

The results of the quantitative analysis of isomeric 1,2-diethyldithioethene mixtures are listed in Table I.

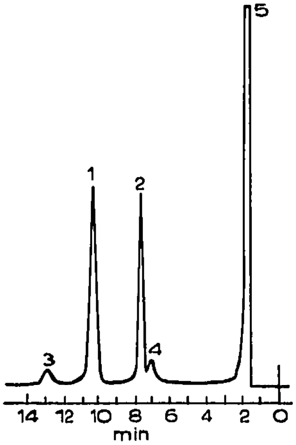
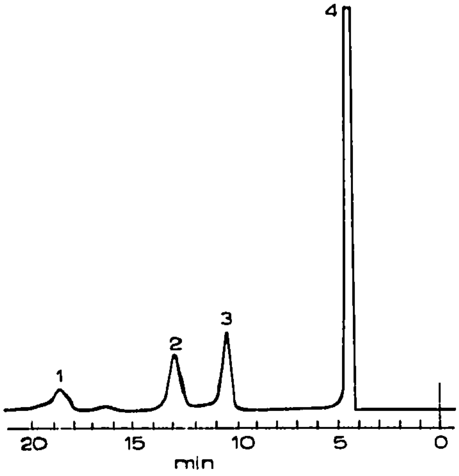


Fig. 1. Chromatogram of a mixture of *cis*- and *trans*-1,2-diethyldithioethene: 1 = *cis*-isomer; 2 = *trans*-isomer; 3 and 4 = unidentified impurities; 5 = *n*-hexane.

TABLE I

QUANTITATIVE ANALYSIS OF MIXTURES OF *cis*- AND *trans*-1, 2-DIETHYLDITHIOETH-ISOMERS

Cis-isomer content in the mixture (%)		*Separation factor,* V_{cis}/V_{trans}
Real	*Found*	
7	6.8	1.33
15	15.6	1.34
55	54	1.32



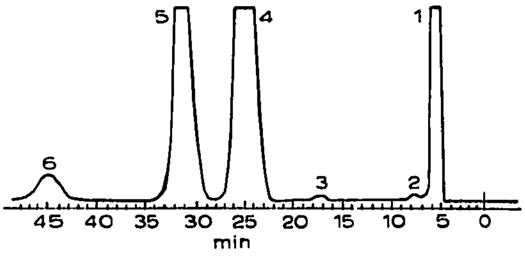


Fig. 2. Chromatogram of a mixture of *cis*- and *trans*-isomers of 1-ethoxy-2-(ethylthio)ethene and glyoxal monothioacetal: 1 = glyoxal monothioacetal; 2 = *cis*-isomer; 3 = *trans*-isomer; 4 = *n*-hexane.

Fig. 3. Preparative-scale separation of *cis*- and *trans*-isomers of 1-ethoxy-2-(ethylthio)ethene and glyoxal monothioacetal: 1 = *n*-hexane; 2 = *n*-heptane; 3 = unidentified impurity; 4 = *trans*-isomer; 5 = *cis*-isomer; 6 = glyoxal monothioacetal.

1-Ethoxy-2-(ethylthio)ethene

A mixture of the *cis* and *trans* isomers of 1-ethoxy-2-(ethylthio)ethene was prepared as a colourless liquid, b.p. 64–66°/14 mm, according to the method of Alkema and Arens[18].

Analytical GC of the *cis*- and *trans*-isomers was carried out using a 3-m long column packed with Chromoton N (0.16–0.2 mm) treated with 1% polyvinylpyrrolidone, impregnated with 10% LAC-3R-728 at 170°. The column efficiency achieved was 3500 theoretical plates. Fig. 3 shows a typical chromatogram obtained. On the basis of the analytical GC results, the preparative-scale GLC separation of the isomers was performed using a 6-m long column at 170°. Chromoton N (0.3–0.4 mm) treated with dimethyldichlorosilane and then impregnated with 2% polyvinylpyrrolidone (mol. wt. 10,000) was used as a solid support. Diethylene glycol succinate (LAC-3R-728; 18%) was choosen as the liquid phase. An example of the chromatograms obtained is shown in Fig. 2. The column efficiency with a sample size of 1 g was 4200 theoretical plates, *i.e.*, more than in the above-mentioned analytical GC. The *cis*-isomer decomposes very rapidly in air, so in order to obtain mixtures of *cis*- and *trans*-1-ethoxy-2-(ethylthio)ethene, the *cis*-isomer, dissolved in carbon tetrachloride, was exposed to UV illumination ($\lambda_{max.} = 254$ nm) in a stream of high-purity argon. After exposure to light, the ratio of isomers was determined by NMR spectrometry as the ratio of vinyl proton signals [in ppm from hexamethyldisiloxane in the field from 4.6 to 6.5 ppm ($J_{cis} = 4.6$ Hz; $J_{trans} = 11$ Hz)]. The accuracy of the NMR analysis was found to be adequate for evaluating the precision of the GLC determination. The results of the quantitative analysis are given in Table II.

TABLE II

QUANTITATIVE ANALYSIS OF MIXTURES OF *cis*- AND *trans*-1-ETHOXY-2-(ETHYLTHIO)ETHENE ISOMERS

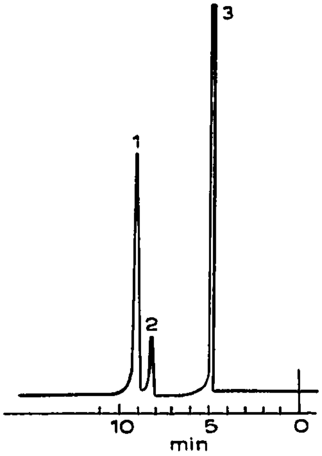
Cis-isomer content in the mixture (%)		*Separation factor,* V_{cis}/V_{trans}
Found by NMR method	*Found by GC method*	
93	90	1.25
22	25	1.24
41	40	1.23
51	50	1.23

1,2-Diphenyldithioethene

cis-1,2-Diphenyldithioethene, m.p. 32–33°, was prepared from 1,2-dichloroethene[19]. A mixture of *cis*- and *trans*-isomers was isolated from the crude reaction product by distillation. Pure *trans*-isomer (m.p. 62–62.5°) was isolated by means of thin-layer chromatography in 3:1 *n*-hexane–benzene.

Attempts to analyze the mixture of *cis* and *trans* isomers of 1,2-diphenyldithioethene using the high-temperature liquid phases SE-30 and Apiezon L, M, N and K were unsuccessful.

Adequate separation was achieved using a 2.8-m long column containing 7% fluorinated polysiloxane SKTFT-50 on silanized Chromosorb W (80–100 mesh) at



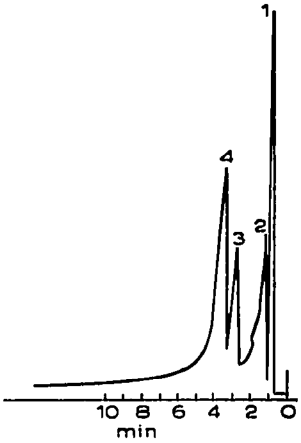


Fig. 4. Separation of the *cis*- and *trans*-isomers of 1,2-diphenyldithioethene: 1 = *cis*-isomer; 2 = *trans*-isomer; 3 = acetone.

Fig. 5. Chromatogram of a mixture of *cis*- and *trans*-isomers of 1-phenylsulphonyl-2-(phenylthio)-ethene: 1 = ethanol; 2 = scale transfer; 3 = *trans*-isomer; 4 = *cis*-isomer.

230°. Fig. 4 shows an example of the chromatograms obtained. The column efficiency was found to be 3500 theoretical plates. The results of the quantitative analysis of isomeric *cis–trans* 1,2-diphenyldithioethene mixtures are given in Table III.

1-Phenylsulphonyl-2-(phenylthio)ethene

cis-1-Phenylsulphonyl-2-(phenylthio)ethene, m.p. 95° (ref. 20), was prepared according to the method of Modena and Todesco[21]. A mixture of *cis*- and *trans*-1-phenylsulphonyl-2-(phenylthio)ethene was obtained by UV irradiation of the *cis*-isomer ($\lambda_{max.}$ = 254 nm), and was separated on a 0.4-m long column with 10% SKTFT-50 liquid phase on Chromosorb W (100–200 mesh) treated with dimethyldichlorosilane at 220°.

An example of the chromatograms obtained is shown in Fig. 5. The column efficiency was 250 theoretical plates and the separation factor was 1.25.

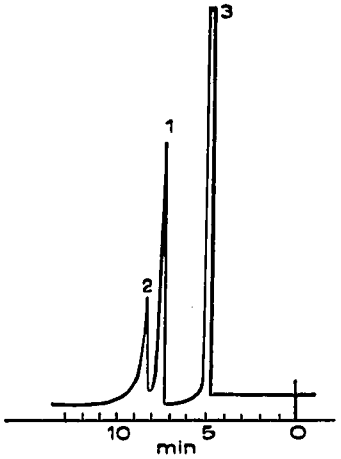
Ethyl ω-styryl sulphide and ethyl ω-styryl sulphone

cis-Ethyl ω-styryl sulphide, b.p. 115–116°/14 mm, and *cis*-ethyl ω-styryl sul-

TABLE III

QUANTITATIVE ANALYSIS OF MIXTURES OF *cis*- AND *trans*-1,2-DIPHENYLDITHIOETHENE ISOMERS

Cis-isomer content in the mixture (%)		*Separation factor,* V_{cis}/V_{trans}
Real	*Found*	
12	11.8	1.23
25	25	1.26
40	41	1.24
60	60.5	1.23



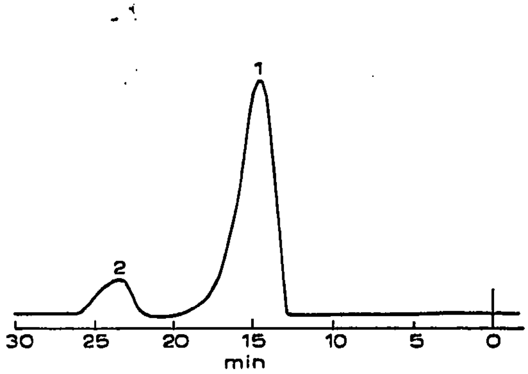


Fig. 6. Chromatogram of a mixture of *cis*- and *trans*-isomers of ethyl ω-styryl sulphone: 1 = *cis*-isomer; 2 = *trans*-isomer; 3 = acetone.

Fig. 7. Separation of *cis*- and *trans*-isomers of ethyl ω-styryl sulphide: 1 = *cis*-isomer; 2 = *trans*-isomer.

phone were prepared according to the method of Truce and Simms[22]. The *cis*- and *trans*-isomers of ethyl ω-styryl sulphone were easily separated at 230° on a 3-m long column packed with dimethyldichlorosilane-treated Chromosorb P (60–80 mesh) impregnated with 10 % SE-30 or SKTFT-50. A higher separation factor was achieved in the case of SE-30. Fig. 6 shows an example of the chromatograms obtained. A column efficiency of 5000 theoretical plates was achieved.

The separation of the *cis* and *trans* isomers of ethyl ω-styryl sulphide was carried out earlier[9] using a 16-m capillary column coated with the tridecyl ether of polyethylene glycol. We were not able to achieve on adequate separation of this mixture by means of gas–liquid chromatography, in spite of numerous attempts with the use of several high-temperature liquid phases in packed columns. However, the separation of these isomers appeared to be possible using a 0.5-m column containing the graphitized carbon black T-168 (specific surface area, 6–8 m^2/g) at 220° and a carrier gas flow-rate of 100 ml/min. A separation factor of 1.55 was obtained.

Graphitized carbon black T-168 was granulated by shaking it in a glass flask for several days, then the material was sieved and the fraction of 0.1–0.25 mm was selected. The packing of the column was carried out very carefully so as to avoid crushing of the particles and the formation of plugs[23]. An example of the chromatograms obtained is shown in Fig. 7.

DISCUSSION

The *cis*-isomers of the α,β-unsaturated sulphur compounds discussed are unstable, tending to isomerize easily or to undergo other chemical transformations. Nevertheless, in this work the possibility of eliminating such chemical transformations in chromatographic analysis has been shown. In order to obtain adequate accuracy, the solid support must be adequately deactivated. Other experimental conditions should be as mild as possible.

In the case of 1-ethoxy-2-(ethylthio)ethenes, the stability of the *cis*-isomer is extremely low and partial isomerization into the *trans*-isomer takes place during distillation at 0.1 mm pressure. It was possible to avoid chemical transformation of this substance by deactivation of the solid support with polyvinylpyrrolidone.

The method permits not only adequate information on the isomer ratio to be obtained, but also high-purity *cis*-isomer to be isolated. On the same column, the chromatography of extremely unstable glyoxal monothioacetal prepared by the reaction of the *cis*-isomer with oxygen[24] was carried out. Attempts to perform such a separation without deactivation of the support were unsuccessful. The isomer ratio changed during the analysis in an irregular manner and glyoxal monothioacetal was irreversively retained in the column. The retention times of the *cis*- and *trans*-isomers were 12 and 10 min, respectively.

In preparative-scale GC of 1-ethoxy-2-(ethylthio)ethene isomers, argon was used as the carrier gas[25,26], which appeared to be convenient. By using traps cooled in liquid nitrogen, all of the carrier gas leaving the column was collected, together with the material separated. After complete elution of the collected fraction, the trap was placed in dry-ice so as to evaporate the argon slowly. A recovery of the material of 85–90% was achieved by means of this collection technique.

In the separation of the *cis*- and *trans*-isomers of ethyl ω-styryl sulphide on a graphitized carbon black column, the substances are likely to elute in accordance with their non-specific intermolecular interaction energy, depending mainly on molecular geometry and orientation on the graphite surface. The energy of non-specific dispersion interaction with graphitized carbon black might be connected with the most advantageous orientation of the molecules towards the basic crystal plane[23].

cis-Ethyl ω-styryl sulphide ($C_6H_5CH{=}CHSC_2H_5$) has a smaller retention volume than the *trans*-isomer, probably due to the close proximity of the SC_2H_5 and C_6H_5 groups, which are not completely coplanar with the plane of the double bond because of steric hindrance. *trans*-Ethyl ω-styryl sulphide is likely to be oriented more easily upon the hexagonal cells on graphitized carbon black, as the SC_2H_5 and C_6H_5 groups might be completely coplanar with the double bond.

For stereoisomeric 1-phenylsulphonyl-2-(phenylthio)ethenes, ethyl ω-styryl sulphides and ethyl ω-styryl sulphones, the adequacy of the quantitative GC determination was confirmed by the analysis of mixtures of a stable standard substance, *viz.*, pentadecane, with a thermally labile *cis*-isomer in which strict proportionality between the detector response and the amount of isomer present was observed.

CONCLUSIONS

The quantitative GC determination of a number of thermally unstable stereoisomeric unsaturated sulphur compounds has been achieved. The *cis*- and *trans*-isomers of ethyl ω-styryl sulphide were easily separated by gas–solid chromatography on a packed column containing the graphitized carbon black T-168.

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