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ALKYLTHIOLATION FOR THE DETERMINATION OF DOUBLE-BOND POSITIONS IN LINEAR ALKENES

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SUMMARY

The iodine-catalysed addition of dimethyl disulphide to linear alkenes leads smoothly to α,β-bis(methylthio)alkanes. These derivatives are stable to gas chromatographic conditions and provide readily recognizable fragments on electron bombardment. This single-step derivatization procedure is thus eminently suitable for the determination of double-bond positions in linear alkenes.

INTRODUCTION

Spectroscopic methods alone fail in all but a few instances in the determination of the position of a double-bond in a hydrocarbon chain[1,2]. The strategy normally adopted in identifying double-bond positions therefore consists of either oxidative cleavage of or addition across the double bond followed by a combination of chromatographic and spectroscopic techniques to identify the products[3–14]. Owing to difficulties in controlling oxidation, particularly when several functional groups are present, addition is normally the preferred procedure.

Various methods have been used to investigate the derivatives formed[3], but the method of choice is combined gas chromatography–mass spectrometry (GC–MS)[7–14]. The criteria for the use of this combination are that the derivatives formed must be stable during GC and that the MS fragmentation be readily interpreted in terms of the original structure.

Direct addition of two identical groups to the double-bond termini provides a single product and thus makes the interpretation of the resulting spectra easier than when unsymmetrical addition yields two structural isomers. Few such symmetrical additions are known, however, and the two simplest, deuteration[7] and methylene insertion[8], give hydrocarbon products and consequent difficulties in interpretation of the mass spectra. A similar, but more involved, procedure which has been much favoured is the conversion of the alkene to the corresponding diol prior to derivatization[9–11]; the diols themselves present difficulties in both GC and MS interpretation.

We have recently shown that oxyselenation provides derivatives of alkenes that are analytically useful for the GC–MS determination of double-bond positions[15]. This, together with the availability of reactive dialkyl disulphides, prompted us to

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look for methods where the disulphides might be added across alkene double bonds.

Literature reports state that dialkyl disulphides add to vinyl sulphide and to styrene in the presence of iodine[16,17]. Iodine catalysis is also effective in promoting the addition of alkyl sulphides to vinyl acetate[18]. Bis(trifluoromethyl) disulphide adds to alkenes photochemically[19]. Hydrogen fluoride has been used as a catalyst for the addition of disulphides to simple alkenes[20].

A simple procedure based on the iodine-catalysed reactions described above[16–18] was adopted for derivatization. The *trans*-isomer of a linear alkene was added to an excess (6 *M*) of dialkyl disulphide, a catalytic amount of iodine (0.05 *M*) added and the resultant solution allowed to stand for 24 h at room temperature. The reaction mixture could then be analysed by GC–MS without further work-up. If it were necessary to store the products for longer periods prior to analysis, the iodine remaining was removed by washing with alkali, to avoid product decomposition.

EXPERIMENTAL

The GC–MS analysis was carried out on a JEOL JCG-20K gas chromatograph coupled directly to a JEOL JMS D-100 mass spectrometer. The gas chromatograms were obtained by recording the total ion current throughout the chromatographic run with the mass spectrometer operating at an electron bombardment energy of 20 eV. The mass spectra themselves were obtained with the machine operating at 70 eV. The column used for chromatography was made of stainless steel, 6 ft. × $\frac{1}{8}$ in. I.D., packed with 10% SE-30 on Chromosorb W AW. Helium at a flow-rate of 30 ml/min was used as the carrier gas.

The *trans*-alkenes used were prepared by Wittig reaction or dehydration, followed by urea adduction[21], and gave satisfactory physical and spectral data in all instances. Iodine and dimethyl disulphide were obtained from E. Merck, (Darmstadt, G.F.R.).

General derivatization procedure

Dimethyl disulphide (6 mmol) and the *trans*-alkene (1 mmol) were placed in a flat-bottomed flask equipped with a magnetic stirrer and iodine (0.05 mmol) was dissolved in the mixture. The flask was purged with nitrogen and closed. After stirring for 24 h at room temperature, reaction was complete.

The product could be subjected directly to GC–MS analysis, but on standing for several days some decomposition occurred. Such decomposition could be avoided by dissolving the product in diethyl ether and washing with dilute aqueous sodium hydroxide.

RESULTS AND DISCUSSION

Reaction conditions

Initial experiments were carried out using either dimethyl or dipropyl disulphide. No differences in yield or in ease of interpretation of the results were found, and as the bis(methylthio) derivatives were more volatile and hence presented an easier GC problem, dimethyl disulphide was used in the systematic investigation.

The amount of iodine used for catalysis did not seem to be critical, although

TABLE I

RETENTION TIMES OF THE BIS(METHYLTHIO)ALKANES PREPARED FROM THE ALKENES STUDIED

Carrier gas, helium; flow-rate, 30 ml/min. Injector temperature, 250°C. Column: stainless steel, 6 ft. × ⅛ in I.D., 10% SE-30 on Chromosorb W AW. Programme: the temperature was increased by 1°C/min from a temperature of 180°C on injection.

Alkene derivatized	*Retention time (min)*	*Alkene derivatized*	*Retention time (min)*
2-Undecene	11.6	1-Tetradecene	29.9
1-Dodecene	18.9	5-Tetradecene	22.1
3-Dodecene	14.6	7-Tetradecene	20.4
6-Dodecene	12.3	1-Pentadecene	36.3
1-Tridecene	23.9	6-Pentadecene	26.3
4-Tridecene	18.0	1-Hexadecene	42.9
		7-Hexadecene	31.5
		8-Hexadecene	31.0

poor results were obtained when much larger or much smaller amounts were used. Ultraviolet irradiation did not appear to improve the reaction yields or rate and was hence not employed.

When higher temperatures (80°C) were used, reaction was complete after 2 h, but the derivative was then contaminated with side-products containing only one methylthio group. A more detailed discussion of this problem will be presented elsewhere[22].

Gas chromatography

GC was carried out on a short packed column (SE-30). Excess of dimethyl disulphide and any remaining alkene were eluted well before the product, which was normally formed cleanly and in good yield (70–90%). The retention times of the derivatives are given in Table I, and it is apparent that they increase with carbon number and as the double bond derivatized nears the chain terminus.

Mass spectrometry

The mass spectra of the derivatives of the three dodecenes studied are given in Fig. 1, and some details of the spectra of the remaining derivatives are given in Table II. The discussion which follows is based on these data.

The mass spectra of the fourteen bis(methylthio)alkanes show considerable uniformity of appearance. In all instances the molecular ion (M) is marked, although the relative intensity decreases from values of about 40% for the derivatives of C_{11} and C_{12} alkenes as the chain length increases. Markedly lower intensities characterize derivatives of terminal alkenes of higher carbon number, *e.g.*, 1-pentadecene and 1-hexadecene. The only other ion observed in the molecular peak region was the considerably less intense M − 47 ion, which is formed by loss of a methylthio radical from the molecular ion.

The low-mass end of the spectra is dominated by hydrocarbon fragments in the series C_nH_{2n-1}. Maximal intensity in this ion series occurs at m/e 55 or 69 (n = 4 or 5) and the former ion provides the base peak ion in all of the C_{15} and C_{16} alkene

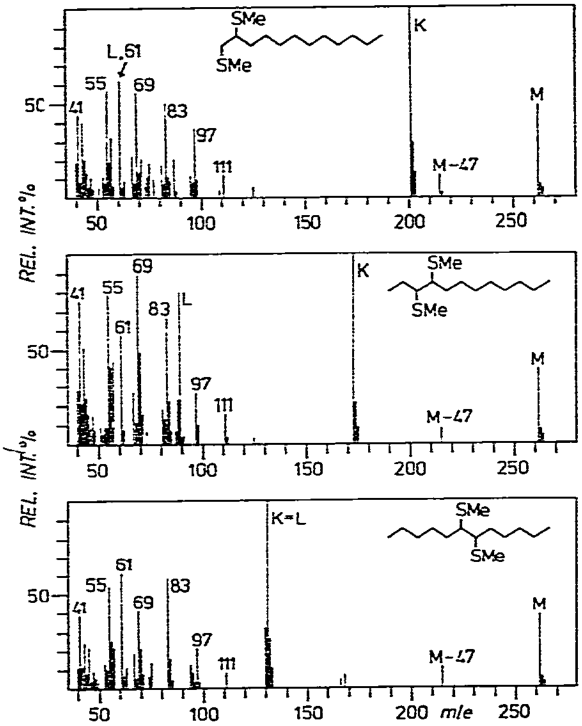

Fig. 1. 70 eV mass spectra of the bis(methylthio)alkanes derived from 1-dodecene, *trans*-3-dodecene and *trans*-6-dodecene. Me = Methyl.

TABLE II

RELATIVE INTENSITIES (%) OBSERVED IN THE MASS SPECTRA OF THE BIS(METHYLTHIO) DERIVATIVES OF ALKENES FOR THE MOLECULAR ION (M), THE CHARACTERISTIC IONS K AND L, AND FOR THE *m/e* 61 ION

Figures in parentheses are *m/e* values. The intensities found for the homologous ion series at *m/e* 41, 55, 69, 83, 97 and 111 are also given.

Alkene derivatized	*M*	*K*	*L*	*m/e*						
				61	*41*	*55*	*69*	*83*	*97*	*111*
2-Undecene	42.3 (248)	100 (173)	57.4 (75)	58.2	50.2	56.2	68.7	52.1	22.3	8.4
1-Dodecene	48.1 (262)	100 (201)	62.2 (61)	62.2	44.3	57.0	56.1	50.4	37.0	12.6
3-Dodecene	39.2 (262)	100 (173)	77.4 (89)	64.2	76.2	79.7	89.2	68.0	27.3	15.5
6-Dodecene	38.6 (262)	100 (131)	L = K	61.9	39.0	54.8	40.5	58.6	21.0	9.1
1-Tridecene	26.9 (276)	100 (215)	70.5 (61)	70.5	69.3	91.0	80.6	78.2	65.4	26.9
4-Tridecene	46.3 (276)	100 (173)	73.3 (103)	75.6	52.2	62.7	68.6	58.2	29.1	13.4
1-Tetradecene	16.2 (290)	83.9 (229)	57.1 (61)	57.1	76.8	100	85.6	78.5	50.1	21.4
5-Tetradecene	45.9 (290)	100 (173)	84.8 (117)	78.4	62.6	76.8	68.2	61.0	40.1	22.2
7-Tetradecene	28.1 (290)	100 (145)	L = K	75.8	67.2	94.3	80.7	67.3	71.8	24.2
1-Pentadecene	10.8 (304)	56.8 (243)	52.6 (61)	52.6	76.3	100	81.6	81.1	57.6	23.7
6-Pentadecene	41.1 (304)	98.4 (173)	92.4 (131)	74.1	83.8	100	96.6	92.8	66.1	40.3
1-Hexadecene	8.7 (318)	41.4 (257)	34.4 (61)	34.4	82.7	100	93.1	92.7	72.4	27.4
7-Hexadecene	31.3 (318)	82.6 (173)	78.2 (145)	66.9	86.9	100	97.3	88.5	79.1	49.5
8-Hexadecene	30.2 (318)	100 (159)	L = K	68.6	52.5	74.4	72.3	56.4	44.9	26.9

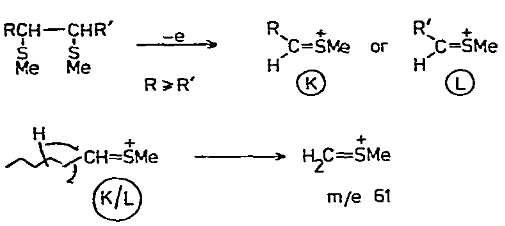

Fig. 2. Origin of the K, L and *m/e* 61 ions in the mass spectra of bis(methylthio)alkanes.

derivatives, except that formed from 8-hexadecene. The marked dominance of the C_nH_{2n-1} ion series over the C_nH_{2n+1} series is probably the result of the ease with which hydrogen transfer to sulphur may take place.

Other ions attracting immediate notice are those due to fragments derived by cleavage through the position of the alkene double bond (see Fig. 2). The ion of higher mass (K) in all instances has greater intensity than the lower mass ion (L), although the difference tends to decrease as the mass difference between K and L decreases. The ion K is sufficiently intense to provide the base peak in the spectra of more than half of the compounds studied.

A further high-intensity ion occurs in the spectra of all of the bis(methylthio)derivatives examined. This ion at *m/e* 61 is presumably due to a rearrangement of the ions K and L such that a hydrogen atom from the alkyl chain is transferred to the carbon atom bearing the charged methylthio moiety, while the hydrocarbon fragment is eliminated as a neutral species, probably as a cycloalkane. It should be noted that this ion arises directly by scission of the chain in terminal alkenes.

In conclusion, the readily identifiable molecular ion, the high intensities of the ions (K and L) due to cleavage of the doubly activated bond formed by derivatization and the general lack of other non-hydrocarbon ions make the mass spectra of the bis(methylthio)alkanes readily usable for the determination of double-bond positions in linear alkenes.

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