DETERMINATION OF DOUBLE-BOND POSITION IN LINEAR ALKENES BY OXYSELENATION AND GAS CHROMATOGRAPHY–MASS SPECTROMETRY

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(Received June 27th, 1977)

SUMMARY

A series of alkenes having different positions of the double bond has been subjected to single-stage conversion into mixed ethers containing oxygen and selenium. The products show characteristic mass-spectral fragmentation, which allows immediate recognition of the original position of the double bond, and are suitable derivatives for gas chromatography–mass spectrometry.

INTRODUCTION

Numerous methods have been described for the determination of double bonds[1,2], but differentiation between alkenes having different positions of the double bond is still an interesting analytical problem. Spectroscopic methods are generally of only limited utility[3,4], and many of the chemical methods are sufficiently complicated as to make their application difficult on a small scale[1,5,6].

The approach currently adopted to this problem is to use a simple derivatisation procedure, followed by gas chromatography–mass spectrometry (GC–MS)[7–14]. This method is very sensitive and is limited only by the difficulty in interpreting the mass spectra.

The manner in which the derivative is obtained may vary greatly, but the net result is always equivalent to addition across the double bond. Generally, addition of X–Y to an unsymmetrical alkene produces two isomeric substituted alkanes, which, on MS, can yield four characteristic ions from cleavage of the bond joining the original double bond termini. When X and Y are identical, a single product yielding two characteristic ions will result. This reaction scheme is slightly modified when the derivatives prepared are cyclic (for example, acetonides and boronates[10,11,14]) in so far as the characteristic ions are the result of cleavage of the bonds immediately adjacent to the original double-bond position.

Pre-requisites for successful interpretation of the mass spectra are that at least one (and preferably both) of the added moieties offers a good locus for charge stabili-

sation, that the combined influence of the substituents is highly directive for fragmentation and that the characteristic ions be readily identifiable. The derivatives typically employed are thus those in which a hetero-atom, normally O or N, is attached to each carbon atom of the original double bond[10–14].

Since oxyselenation[15,16] leads to the attachment of one Se and one O atom to the double-bond termini, and both Se and O are good charge stabilisers in MS fragmentation, we decided to investigate the analytical utility of this procedure. The method seemed particularly attractive because the Se-containing fragments would be easily identified in the mass spectra as a result of the isotopic abundances of that element (^{74}Se: ^{76}Se: ^{77}Se: ^{78}Se: ^{80}Se: ^{82}Se = 0.87: 9.02: 7.58: 23.52: 49.82: 9.19 %).

The procedure adopted for preparation of the derivatives was essentially that of Sharples and Lauer[15]. The organic diselenide, in a suitable solvent, was treated with bromine to generate the corresponding organic selenyl bromide *in situ*. When the alkene was added, *immediate addition across the double bond occurred*, and this was followed by a slower solvolysis step to give the final product (see Scheme 1). When methanol was used as solvent, no base was required to encourage solvolysis, but when the solvent was acetic acid, potassium acetate was added. The reaction was quenched by the addition of water and ethyl acetate; the ethyl acetate layer was then washed with sodium carbonate solution and dried with sodium sulphate and the solvent was removed under reduced pressure. The derivative was subjected to GC–MS without further purification.

RESULTS AND DISCUSSION

Choice of selenyl derivative

Four derivatives of 6-dodecene were prepared initially in order to examine their suitability for GC–MS:

RCH (SePh) . CH(OAc)R   (A)
RCH(SePr^i) . CH(OAc)R   (B)
RCH(SePh) . CH(OMe)R   (C)
RCH(SePr^i) . CH(OMe)R   (D)
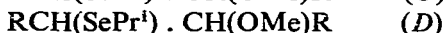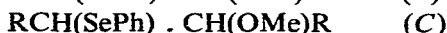
The mass spectra of the derivatives A and B were typified by losses of acetic acid fragments, and other elimination reactions were plentiful. The position was further complicated by the thermal instability of these derivatives and the consequent difficulties encountered in GC. The derivative C was eluted substantially unchanged
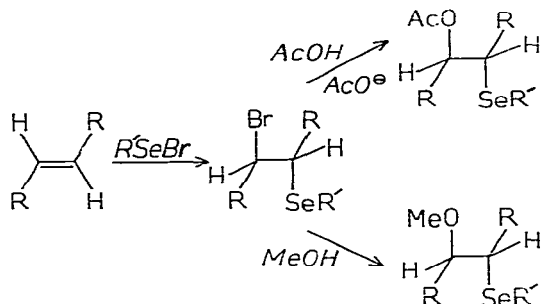
Scheme 1. Oxyselenation of a symmetrical alkene[15].

TABLE I

RETENTION TIMES OF MSP-DERIVATIVES

Conditions for GLC: carrier gas, helium (35 ml/min); injector temperature, 250°; column, stainless steel (6 ft. × 1/8 in.), 10% of SE-30 on Chromosorb W/WA; temp. programme, initially 220°, then 1°/min.

Alkene derivatised	Retention time (min)	Alkene derivatised	Retention time (min)
2-Undecene	10.0	7-Tetradecene	19.8
1-Dodecene	17.6	1-Pentadecene	35.8
3-Dodecene	12.6	6-Pentadecene	24.4
6-Dodecene	11.2	7-Pentadecene	24.1
1-Tridecene	23.6	1-Hexadecene	41.9
4-Tridecene	15.4	7-Hexadecene	28.7
1-Tetradecene	29.7	8-Hexadecene	28.3

from the gas chromatograph and provided a mass spectrum that could be interpreted in terms of the original double-bond position. The final derivative, D, as well as being stable during GC, yielded a spectrum largely accountable in terms of fragmentation through the central bond. Thus, derivative D was chosen for further investigation, on the basis that it was of lower mass than C and hence more volatile. The mixed methoxy-isopropyl-selenyl ethers (MSP-derivatives) of fourteen linear alkenes were prepared, and their fragmentation was studied.

Gas chromatography

A short column packed with SE-30 was used throughout. This was partly because of the thermal sensitivity of the various selenyl ethers, but also because we regarded separation (unless it was complete) of the isomeric ethers derived from a single alkene as a disadvantage. Apart from unreacted starting materials and their decomposition products, GC showed only the presence of the expected derivatives in yields of up to 90%. The retention times of the MSP-derivatives (see Table I) increased with increasing chain length and as the double bond neared the terminal position.

Mass spectrometry

The mass spectra of the MSP-derivatives all showed marked molecular ions, relative intensity about 20%, and comparatively few high-mass fragments. Examination of these latter fragments showed that the expected two isomers were indeed formed from all but symmetrical alkenes, which yielded a single product. The spectra of four typical MSP-derivatives are shown in Fig. 1.

The ions arising from cleavage through the original double bond (in the derivatives, a doubly-activated single bond) are indicated in Scheme 2. The Se-containing fragments V and W are readily identified in the mass spectra by the isotopic distribution associated with Se. Normally, V and W are accompanied by the species $V + 1$ and $W + 1$ and thus give rise to an easily recognisable set of ions. The origin of the $V + 1$ and $W + 1$ ions presumably involves transfer of H from a position at some distance from the chain-bond being cleaved, as such an ion is only observed when the excised methoxy-containing radical contains at least three carbon atoms from the original chain, *i.e.*, a position such that at least six atoms are involved in the process.
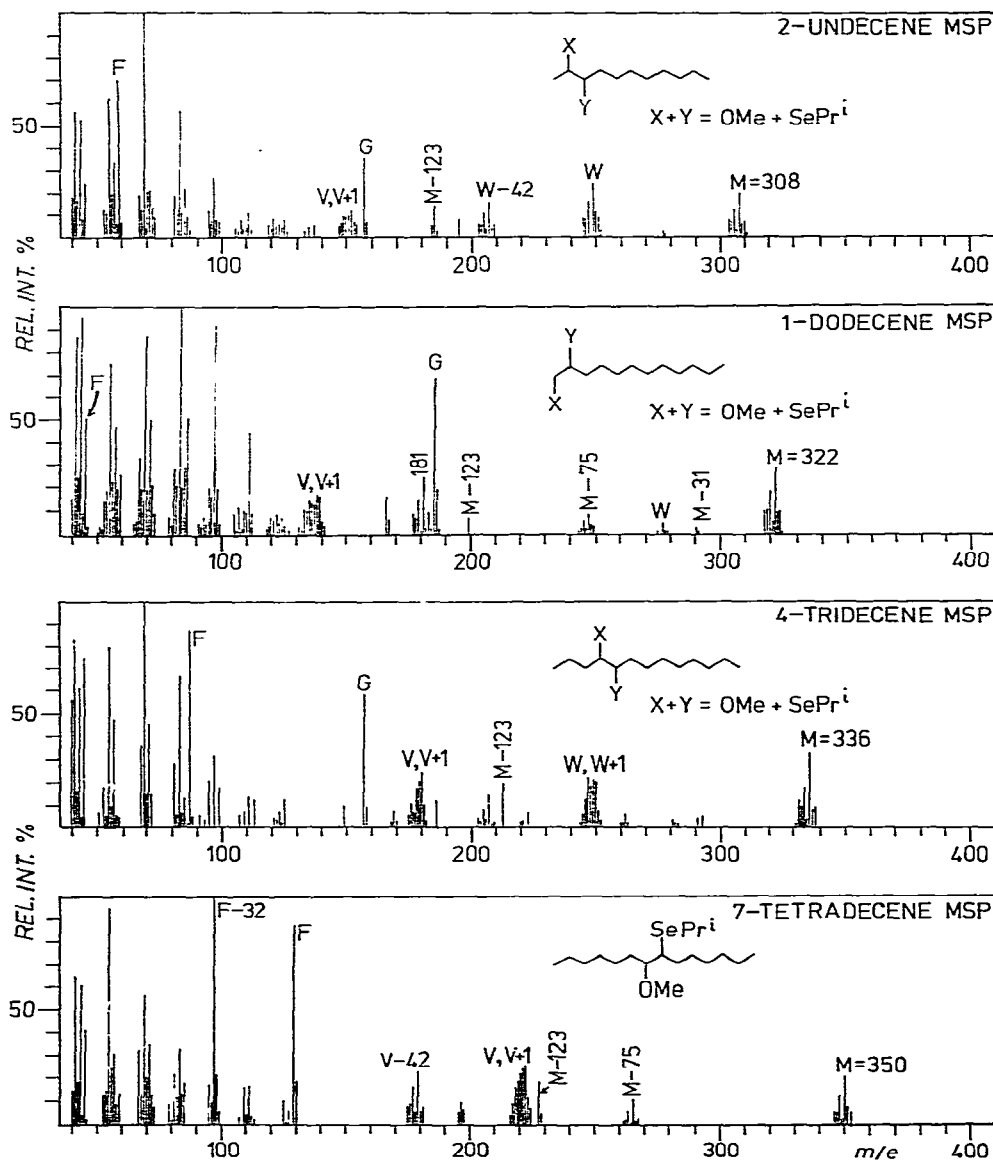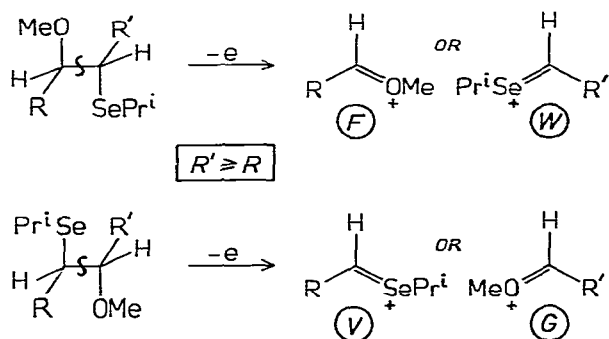
Fig. 1. The 70-eV mass spectra of MSP-derivatives of 2-undecene, 1-dodecene, 4-tridecene and 7-tetradecene.

The methoxy-fragment ions (F and G) normally provide the most intense non-hydrocarbon species in the spectrum and are thus easily detected. The hydrocarbon ions show the distribution of intensities expected in simple hydrocarbons[17], except where F (or G)—32 mass-unit ions (the result of methanol elimination from F or G) give enhanced intensities. The only other ions of frequent occurrence are associated with loss of a methoxy-radical (M—31), a methoxy-radical plus propane (M—75) and of

Scheme 2. Provenance of the ions F, G, V and W in the mass spectra of MSP-derivatives of alkenes.

the isopropylselenyl radical (M—123), and these cause no difficulty in interpreting the spectra.

The only instances in which the ions F, G, V and W may be difficult to identify are in the MSP-derivatives of terminal alkenes for which the ions (F and W in Scheme 2) resulting from cleavage in the MSP-isomer having Se in the 2-position are weak: this we attribute to the relative dominance of the MSP-isomer with Se in the 1-position as a result of regiospecificity during derivatisation (see ref. 18). On the other hand, the MSP-derivatives of 1-alkenes show a characteristic Se-containing ion at m/e 181, attributable to cleavage through the C_2–C_3 bond. The relative intensities of the ions are shown in Table II.

TABLE II

RELATIVE INTENSITIES FOR MOLECULAR ION (M), IONS F, G, V and W AND THAT AT m/e 181 FOR MSP-DERIVATIVES

The relative intensities of the Se-containing ions (M, V, W and m/e 181) are not corrected for the isotopic distribution of this element. The figures in parentheses are m/e values.

| Alkene derivatised | Relative intensities of ions (%) | | | | | |
	M	F	G	V	W	m/e 181
2-Undecene	20.6 (308)	70.0 (59)	36.5 (157)	10.0 (151)	25.6 (249)	—
1-Dodecene	29.6 (322)	51.8 (45)	70.1 (195)	14.4 (137)	4.6 (277)	25.9
3-Dodecene	18.7 (322)	65.5 (73)	42.0 (157)	12.0 (165)	15.5 (249)	—
6-Dodecene*	21.8 (322)	100 (115)	100 (115)	27.4 (207)	27.4 (207)	—
1-Tridecene	23.9 (336)	27.3 (45)	86.4 (199)	10.7 (137)	4.7 (291)	19.1
4-Tridecene	33.0 (336)	88.0 (87)	59.5 (157)	21.5 (179)	20.3 (249)	—
1-Tetradecene	25.4 (350)	45.6 (45)	64.0 (213)	16.5 (137)	1.3 (305)	26.8
7-Tetradecene*	23.8 (350)	88.0 (129)	88.0 (129)	25.0 (221)	25.0 (221)	—
1-Pentadecene	26.5 (364)	44.5 (45)	64.0 (227)	16.0 (137)	4.3 (319)	29.4
6-Pentadecene	21.0 (364)	75.0 (115)	45.0 (157)	26.0 (207)	20.0 (249)	—
7-Pentadecene	19.1 (364)	53.5 (129)	47.0 (143)	17.0 (221)	17.0 (235)	—
1-Hexadecene	29.8 (378)	42.6 (45)	67.8 (241)	18.0 (137)	6.5 (333)	36.5
7-Hexadecene	18.7 (378)	54.5 (129)	39.0 (157)	16.2 (221)	15.0 (249)	—
8-Hexadecene*	11.2 (378)	89.5 (143)	89.5 (143)	31.1 (235)	31.1 (235)	—

* Symmetrical alkenes, for which the ions $F = G$ and $V = W$.

EXPERIMENTAL

The GC–MS was carried out on a JEOL JGC-20K gas chromatograph directly coupled to a JEOL JMS D-100 mass spectrometer. The total-ion-current monitor was used with the mass spectrometer operating at 20 eV when recording the gas chromatograms, and the mass spectra were obtained at 70 eV. The GC was carried out on a stainless-steel column (6 ft. × 1/8 in.) packed with 10% of SE-30 on Chromosorb W (AW), with helium as carrier gas (flow-rate 35 ml/min). The *trans*-alkenes used were prepared by the Wittig reaction or by dehydration, followed by urea-adduct formation[19,20], and gave satisfactory physical data in all cases. Diphenyl diselenide (purum grade) was the commercial product from Fluka (Buchs, Switzerland) and di-isopropyl diselenide was obtained by the procedure of Rebane[21].

7-Acetoxy-6-(phenylseleno)dodecane (A)

Bromine (0.80 g, 0.5 mmol) in glacial acetic acid (1.4 ml) was added to diphenyl diselenide (0.17 g, 0.54 mmol), and the mixture was stirred for 15 min at room temperature; a homogeneous dark-red solution was obtained. *trans*-6-Dodecene (0.168 g, 1 mmol) and anhydrous potassium acetate (0.196 g, 2 mmol) were then added. There was an immediate exothermic reaction, and a pale-yellow suspension was obtained. After stirring this for 1 h, water (2 ml) and ethyl acetate (5 ml) were added, the ethyl acetate layer was separated, and the aqueous layer was extracted with two further 5-ml portions of ethyl acetate. The combined extracts were washed with water (2 × 10 ml) and 10% aqueous sodium carbonate (10 ml) and finally dried over sodium sulphate. After removal of the ethyl acetate under reduced pressure, the product was dissolved in chloroform and used directly for GC–MS. In the 70-eV mass spectrum of A, the major peaks observed [with the m/e value and intensity (%) shown in parentheses] were: M (384; 12), M—HOAc (324; 18), M—C_5H_{11} (313; 11), Ph_2Se (234; 49), M—SePh (227; 32), M—SePh—CH_2CO (185; 34), SePh (147; 33) and 79 (100).

7-Acetoxy-6-(isopropylseleno)dodecane (B)

The procedure was as for A, except that di-isopropyl diselenide was used in place of diphenyl diselenide. In the 70-eV mass spectrum of B, the major peaks observed, and their relative intensities, were: M (350; 11), M—HOAc (290; 17), M—HOAc—Pr (247; 16), M—SePr (227; 9), M—SePr—CH_2CO (185; 14), and 79 (100).

7-Methoxy-6-(phenylseleno)dodecane (C)

The procedure was as for A, except that methanol was used instead of acetic acid, the addition of potassium acetate was omitted, and the mixture was set aside overnight rather than worked up after 1 h. In the 70-eV mass spectrum of C, the major peaks and their relative intensities were: M (356; 18), M—Pr (313; 8), V (241; 11), Ph_2Se (134; 15), SePh (147; 29), F (115; 86), and 55 (100).

7-Methoxy-6-(isopropylseleno)dodecane (D)

The procedure was as for C, but di-isopropyl diselenide was used in place of diphenyl diselenide. In the 70-eV mass spectrum the major peaks and their relative intensities were: M (322; 22), V (207; 27), M—123 (199; 17), and F (115; 100).

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