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GAS CHROMATOGRAPHY IN THE IDENTIFICATION OF POSITIONAL AND GEOMETRICAL ISOMERS OF COMPLEX C_8–C_{13} *n*-ALKENE MIXTURES FROM THE "OLEX" PROCESS

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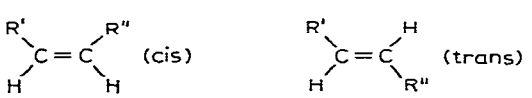
SUMMARY

A comparative study has been made of different methods of separation of the components of mixtures of *n*-alkenes in the C_8–C_{13} range obtained by the "Olex" process. The analyses have been carried out by capillary column gas–liquid chromatography, complementary data being obtained by gas chromatography–mass spectrometry and infrared spectroscopy.

INTRODUCTION

Among the most widely used raw materials utilized by the producers of "detergent alkylates", alkylphenols and oxoalcohols, *n*-olefins from the Olex process are gaining in popularity. These compounds are typically synthesized by noble metal catalyzed dehydrogenation of C_8–C_{10}, C_{10}–C_{13}, C_{11}–C_{14} and C_{15}–C_{18} *n*-alkanes. The dehydrogenation product still contains a large amount of unreacted *n*-alkanes. Enrichment in *n*-alkenes is achieved by selective adsorption of the olefins on molecular sieves and subsequent displacement with a polar solvent, in the "Olex" process. Apart from other impurities (alkanes, aromatics, dienes), *n*-monoalkene double bonds are located in non-specific positions and the relative amounts of *cis*- and *trans*-isomers formed are very variable. From the analytical point of view, the determination of both the geometry and the position of the double bond is complicated, since the *n*-monoalkene samples typically comprise complex mixtures of a wide range of carbon numbers and relatively high molecular weight. All possible positional and geometrical isomers are present:



R′ and R″ = linear alkyl chains

Structural determinations of alkenes of low molecular weight have been described by several workers[1–4]. There have been few studies of higher *n*-alkenes (C_8). The usual oxidative methods of double-bond cleavage with ozone or other oxidants and gas chromatographic (GC) determination of the resulting acids[5–7] may be used only after separation of the mixture into fractions of single carbon number, in order to overcome difficulties in the interpretation of the results. Moreover, this analytical procedure is lengthy and does not allow a determination of the quantity of the geometrical isomers. For similar reasons, nuclear magnetic resonance spectroscopy[8] cannot be directly employed for the analysis of these mixtures. Other workers have transformed compounds containing single double bonds into epoxides or vicinal dibromoalkanes[9,10], or into diols followed by condensation of the diols with acetone to form the corresponding cyclic ketals[11] or cyclic boronate esters[4,12]. All these methods are generally not suited to the resolution of this problem because of the presence of many different isomers and carbon numbers. As shown in Table I, an increase of the molecular weight and of the carbon number range increases the number of possible positional and geometrical isomers.

TABLE I

NUMBER OF POSITIONAL AND GEOMETRICAL *n*-MONOALKENE ISOMERS OF DIFFERENT CARBON NUMBER AND COMPOSITE CUTS

Carbon number	*Positional isomers*	*No. of cis-/trans- plus α positions*
C_8	$\alpha, \beta, \gamma, \delta$	7
C_9	$\alpha, \beta, \gamma, \delta$	7
C_{10}	$\alpha, \beta, \gamma, \delta, \varepsilon$	9
C_{11}	$\alpha, \beta, \gamma, \delta, \varepsilon$	9
C_{12}	$\alpha, \beta, \gamma, \delta, \varepsilon, \zeta$	11
C_{13}	$\alpha, \beta, \gamma, \delta, \varepsilon, \zeta$	11
C_{14}	$\alpha, \beta, \gamma, \delta, \varepsilon, \zeta, \eta$	13
C_8–C_{10}	α to ε	23
C_{10}–C_{13}	α to ζ	40

The search for a method of separation and identification of all the mixture components has led to a comparative study based upon the GC analysis of (A) chlorinated alkenes, (B) bis(trimethylsilyl) derivatives of the vicinal diols obtained by oxidation with osmium tetroxide, (C) trimethylsilyl derivatives of the products obtained by oxidation of the olefins with hydrogen peroxide, (D) untreated alkene mixtures and of the separated *trans*- and *cis*-fractions. The lack of available, pure high-molecular-weight alkene isomers as standards for the required determinations did not allow a direct identification, and accuracy data for the quantitative determinations could not be obtained. Therefore indirect methods of determination were used. The identification of the alkene derivatives was performed by GC–mass spectrometry (MS), and the results obtained from different methods have been compared in order to obtain a means for complete fitting of the data. A previous separation[13] of the *cis*- and *trans*-fractions has been of great assistance, both in identification and in comparison purposes. Gas chromatographic retention times and mass spectra of some alkene derivatives are reported.

EXPERIMENTAL

Preparation of the alkene derivatives

Chlorination. Chlorine, produced by the reaction of concentrated hydrochloric acid with manganese dioxide, diluted with nitrogen and dried by passing through 98% sulphuric acid, was allowed to react with a 1:200 (v/v) mixture of *n*-alkenes with carbon tetrachloride in a cylindrical Drechsel equipped with an efficient gas diffuser. The unreacted chlorine was passed into a solution of sodium hydroxide. The reaction required 5 min, a consumption of *ca.* 10–20 ml HCl and gas flow-rates (nitrogen plus chlorine) of *ca.* 300 ml/min. At the end of this time a light yellow colour had appeared in the reaction mixture. Too strong oxidation conditions produced visibly darker colours. After evaporation of the solvent the sample was directly injected into the gas chromatograph. The reaction time and conditions were tested by chlorination and GC of α-alkene standards and *cis*-/*trans*-fractions in order to verify the reaction yield and selectivity.

Oxidation with osmium tetroxide. A 20-μl volume of the alkenes and 100–120 mg of pure OsO_4 (Carlo Erba, Milan, Italy) were added to 5 ml of diethyl ether in a 15-ml flask equipped with a magnetic stirrer. The reaction was carried out for 40 min with swirling. A saturated solution (5–10 ml) of sodium sulphite in water was then added and the two-phase mixture was vigorously swirled for 2 h. After the addition of NaCl, the organic phase was isolated, dried, evaporated to small volume, diluted with one drop of pyridine and allowed to react with 0.1 ml of trimethylchlorosilane and 0.3 ml of hexamethyldisilazane (Carlo Erba) for 20–30 min at *ca.* 35°. After slight and careful concentration, the mixture was injected into the gas chromatograph.

This procedure is a modification of that reported by other workers[4,11] for alkenes and unsaturated fatty esters. The reaction yield was controlled by GC, by observing the presence of low-boiling degradation products. The selectivity for the positional and geometrical isomers was measured with standard α-alkenes and with some *trans*- and *cis*-fractions of known composition for the positional and geometrical isomers.

Oxidation with hydrogen peroxide. To 2 ml of alkenes were added 15 ml of diethyl ether and 20–50 mg of osmium tetroxide in an Erlenmeyer flask fitted with a magnetic stirrer and condenser. After swirling for a few minutes, 15 ml of 36% hydrogen peroxide were added and allowed to react under swirling for 1 h (the reaction time was dependent on the amount of OsO_4 added). The phases were separated when the colour of the organic phase turned to yellow-green. The organic phase was carefully treated by dropping from the top of the condenser a saturated sodium sulphite solution until the aqueous phase darkened. The organic phase was then isolated, dried, evaporated and a small quantitaty of the residue silylated as described in *oxidation with osmium tetroxide* but with a shorter reaction time. The silylated products were injected into the gas chromatograph. The oxidation reaction can be written as follows:

$$R'\text{–}CH\text{=}CH\text{–}R'' \xrightarrow[OsO_4]{+H_2O_2} R'\text{–}\underset{\displaystyle OH}{\underset{|}{CH}}\text{–}\underset{\displaystyle OH}{\underset{|}{CH}}\text{–}R'' + R'\text{–}\underset{\displaystyle O}{\underset{\|}{C}}\text{–}\underset{\displaystyle OH}{\underset{|}{CH}}\text{–}R'' + R'\text{–}\underset{\displaystyle OH}{\underset{|}{CH}}\text{–}\underset{\displaystyle O}{\underset{\|}{C}}\text{–}R'' \quad (1)$$

The reaction products were analyzed by GC and GC–MS.

Separation of the alkene mixtures into the trans-, cis- and α fractions

Alkene (C_8–C_{10} and C_{10}–C_{13}) mixtures were separated into the *trans-*, *cis-* and α fractions by column chromatography on an alumina–silver nitrate support. The procedure of Chapman and Kuemmel[13] was followed. A separate analysis of both the *cis-* and *trans-*fractions was carried out by GC and infrared (IR) spectroscopy. These fractions were also separately derivatized to the corresponding diols or dichlorides by the above methods and analyzed by GC and IR spectroscopy in order to obtain support for the qualitative and quantitative determinations.

GC, MS and IR spectroscopy

Unless indicated otherwise, the reported GC analyses were carried out using a 100 m × 0.25 mm I.D. stainless-steel capillary column (1:100 inlet splitter ratio) coated with DC-550 (phenylmethylsilicone oil). The injector and detector temperatures were maintained at 300° for all measurements. A Carlo Erba GI gas chromatograph equipped with flame ionization detector was used. GC–MS analyses were performed by coupling a Varian 2700 gas chromatograph with a Varian CH5 mass spectrometer equipped with a single-stage Biemann–Watson separator[14] and electron-impact ion source operating at 250° and an ionization potential of 18 eV. IR spectra were obtained with a Perkin-Elmer 377 spectrophotometer.

Analyzed samples

C_8–C_{10} and C_{10}–C_{13} mixtures, pure single-carbon-number cuts and the corresponding derivatives were analyzed. Standard samples of *cis-* and *trans-*fractions were also determined.

RESULTS

The presence of numerous components in the alkene mixtures is shown by the chromatograms of both the underivatized and derivatized compounds. In particular, the direct injection of the C_8–C_{10} and C_{10}–C_{13} *n*-monoalkenes leads to the separation of only a few compounds (Fig. 1). It was found that a change of column polarity did not enhance the separation (see also Table II). As shown in Fig. 2 the best resolution is achieved by carrying out a preliminary isolation of the *trans-* and *cis-*isomers.

From the available boiling-point data of the pure substances (see Table II for C_8 alkenes), the *β-cis-*isomer has the highest boiling point and retention time for each carbon number, followed by the *β-trans-*isomer. The separation of the most internal positions is not complete and sufficient resolution cannot be obtained for carbon numbers $>C_8$. As observed by other workers and shown in Table II, the GC behaviour of the α positions is singular, the retention times and boiling points being similar to those of the most internal positions. Moreover, the polarity of the column does not influence greatly the relative retention times of the α-positions. From the point of view of a comparison between methods, the analysis of the underivatized alkenes by GC provides useful reference points for some quantitative data obtained for a single component using the other reported methods of chlorination and oxidation. The direct GLC analysis of the *n*-monoalkenes, in fact, does not need derivatization steps. Reliability is, therefore, high; however, component separation is poor.

The substitution of the double bond with two –Cl or $-OSi(CH_3)_3$ groups in-

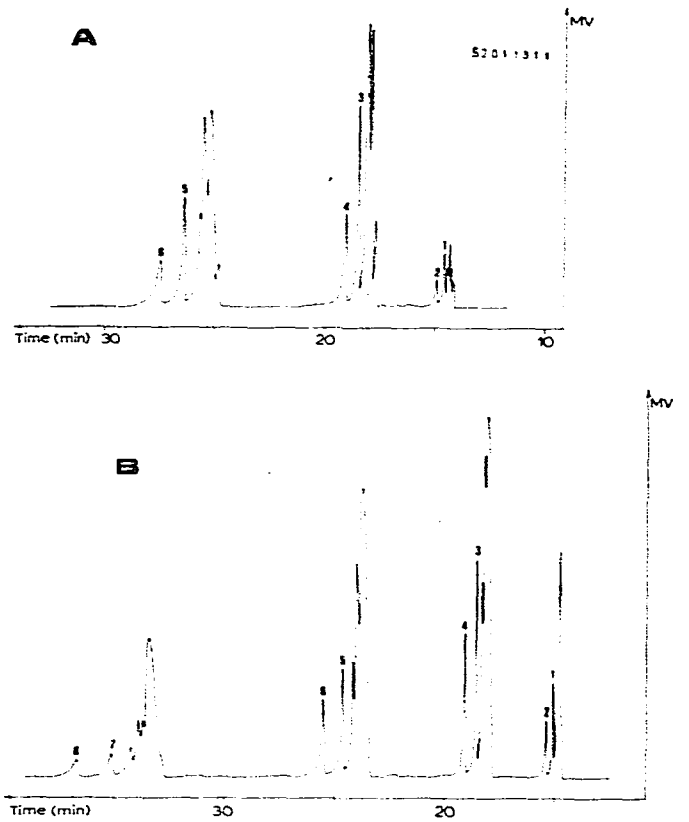


Fig. 1. Capillary column gas chromatograms of *n*-alkenes. Peaks in chromatogram A: 1 = *β-trans*-octene; 2 = *β-cis*-octene; 3 = *β-trans*-nonene; 4 = *β-cis*-nonene; 5 = *β-trans*-decene; 6 = *β-cis*-decene. Peaks in chromatogram B: 1 = *β-trans*-decene; 2 = *β-cis*-decene; 3 = *β-trans*-undecene; 4 = *β-cis*-undecene; 5 = *β-trans*-dodecene; 6 = *β-cis*-dodecene; 7 = *β-trans*-tridecene; 8 = *β-cis*-tridecene. Peaks not listed here refer to *n*-alkenes with different double-bond positions (see Table II). Isothermal conditions: oven temperature, 90° for A and 110° for B. Carrier gas: nitrogen. Flow-rate: 1 ml/min.

fluences greatly the GC retention times of geometrical and positional isomers, the structural differences being emphasized. In particular, the retention times of the *α*-position are very sensitive to di-substitution: the ratio between the retention times of *α*- and of *β-cis* increases as the molecular weight of the substituent increases (see Table III) (ignoring other factors such as the "polarities" of the substituents and of the column).

Gas chromatograms of the dichlorides are shown in Fig. 3. The retention times of unresolved components are shown in Table IV.

The overlapping of components has been resolved by isolating the *trans*- or/and *cis*-fractions. A change of GC column polarity [poly(phenyl ether)coating] does not result in any improvement in component resolution. However, the effectiveness of the direct analysis of C_8–C_{10} and C_{10}–C_{13} chlorinated alkenes by GC under the described conditions can be evaluated respectively as $^{19}/_{23}$ and $^{32}/_{40}$ resolved components.

Component resolution can be enhanced by transformation of the alkenes into

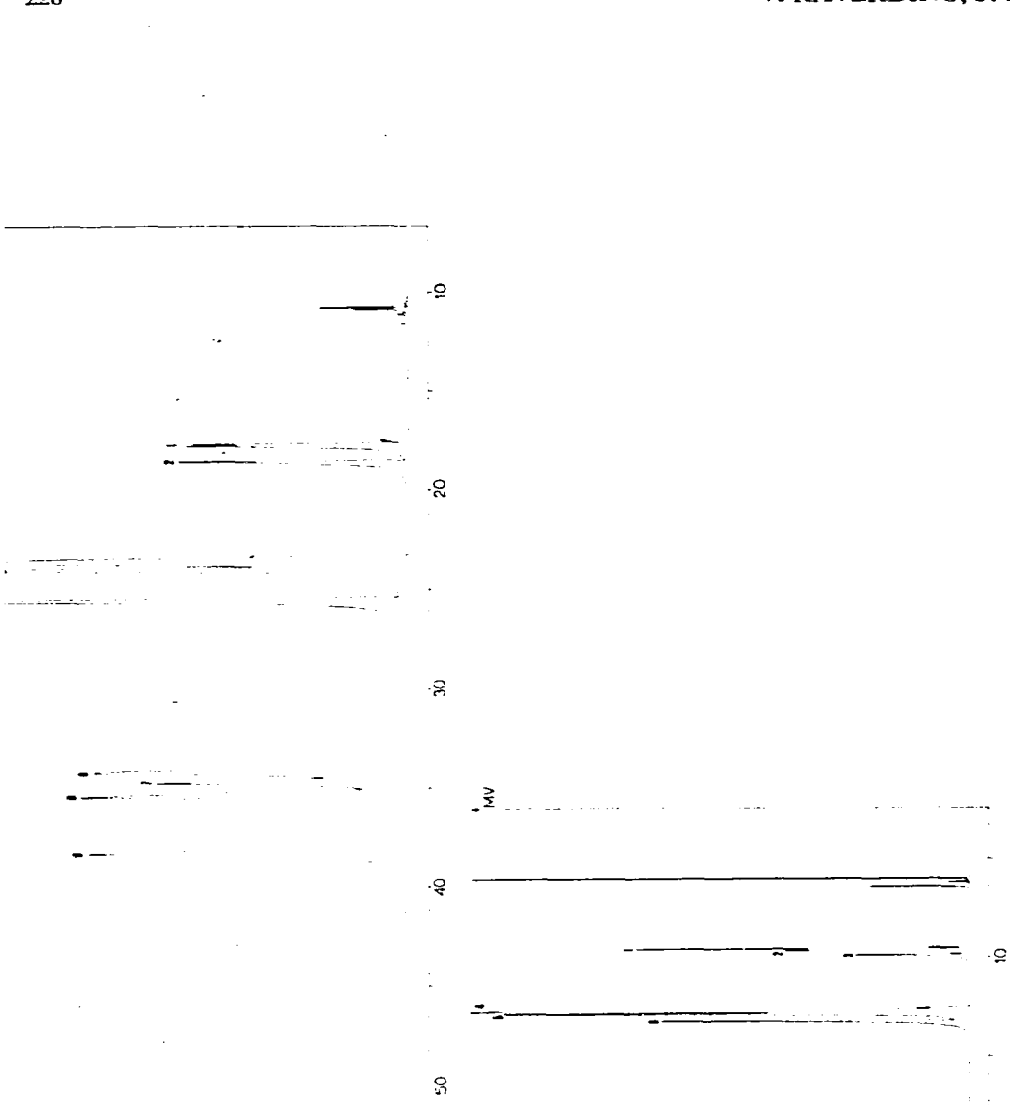


Fig. 2. Capillary column gas chromatograms of the *trans*- and *cis*-fractions of a mixture of C_{10}–C_{13} *n*-alkenes. Peaks in chromatogram A: *cis*-alkenes, 1 = [γ + (δ + ε)]-decene; 2 = β-decene; 3 = (δ + ε)-undecene; 4 = γ-undecene; 5 = β-undecene; 6 = (ε + ζ)-dodecene; 7 = δ-dodecene; 8 = γ-dodecene; 9 = β-dodecene; 10 = (ε + ζ)-tridecene; 11 = δ-tridecene; 12 = γ-tridecene; 13 = β-tridecene. Peaks in chromatogram B: *trans*-alkenes, 1 = (δ + ε)-decene; 2 = γ-decene; 3 = β-decene; 4 = (δ + ε)-undecene; 5 = γ-undecene; 6 = β-undecene; 7 = (δ + ε + ζ)-dodecene; 8 = γ-dodecene; 9 = β-dodecene; 10 = (δ + ε + ζ)-tridecene; 11 = γ-tridecene; 12 = β-tridecene. Isothermal conditions: oven temperature, 110° for both chromatograms.

TABLE II

BOILING POINTS AND NET RETENTION TIMES OF C_8 *n*-MONOALKENES

Position	*Boiling point** (*°C at 760 mm Hg*)	*Net retention time*		
		*Gal***	*Column DC 550*	*PPE****
α	121.3	0.828	0.801	0.780
β-cis	125.6	1.000	1.000	1.000
β-trans	124.9	0.948	0.907	0.923
γ-cis	123.2	0.914	0.874	0.813
γ-trans	123.3		0.841	
δ-cis	122.7	0.828	0.827	0.780
δ-trans	122.4		0.801	

* Literature data.
** Capillary column coated with gal (Apiezon grease; 50 m × 0.25 mm I.D.).
*** Capillary column coated with poly(phenyl ether) (6 rings) (25 m × 0.25 mm I.D.).

TABLE III

RATIO BETWEEN THE RETENTION TIMES OF *α*- AND *β-cis* DI-SUBSTITUTED AND UNSUBSTITUTED POSITIONS OF *n*-OCTENE

Substituents	*α-/β-cis ratio*
Unsubstituted	0.801
–Cl	1.117
$-OSi(CH_3)_3$	1.304

TABLE IV

RETENTION TIMES (IN ARBITRARY UNITS) OF THE DICHLORIDES FROM C_8–C_{13} *n*-MONOALKENES

Position	*Carbon number*					
	8	*9*	*10*	*11*	*12*	*13*
α	339	552	883	1328	2005	3028
β-cis	288	471	758	1152	1740	2615
β-trans	264	435	707	1079	1633	2452
γ-cis	276	453	728	1107	1672	2508
γ-trans	252	411	672	1028	1553	2327
δ-cis	252	420	672	1028	1553	2327
δ-trans	243	387	629	960	1457	2186
ε-cis			672	575	1503	2243
ε-trans			629	938	1424	2130
ζ-cis					1503	2214
ζ-trans					1424	2090

silylated diols (oxidation with osmium tetroxide) and followed by GC. Gas chromatograms of derivatized C_8–C_{10} and C_{10}–C_{13} *n*-alkene mixtures and of the respective *cis*- and *trans*-fractions are shown in Fig. 4. Retention times for each component are given in Table V. This determination provides a separation of all and 37 of the 40 components respectively for the C_8–C_{10} and C_{10}–C_{13} fractions.

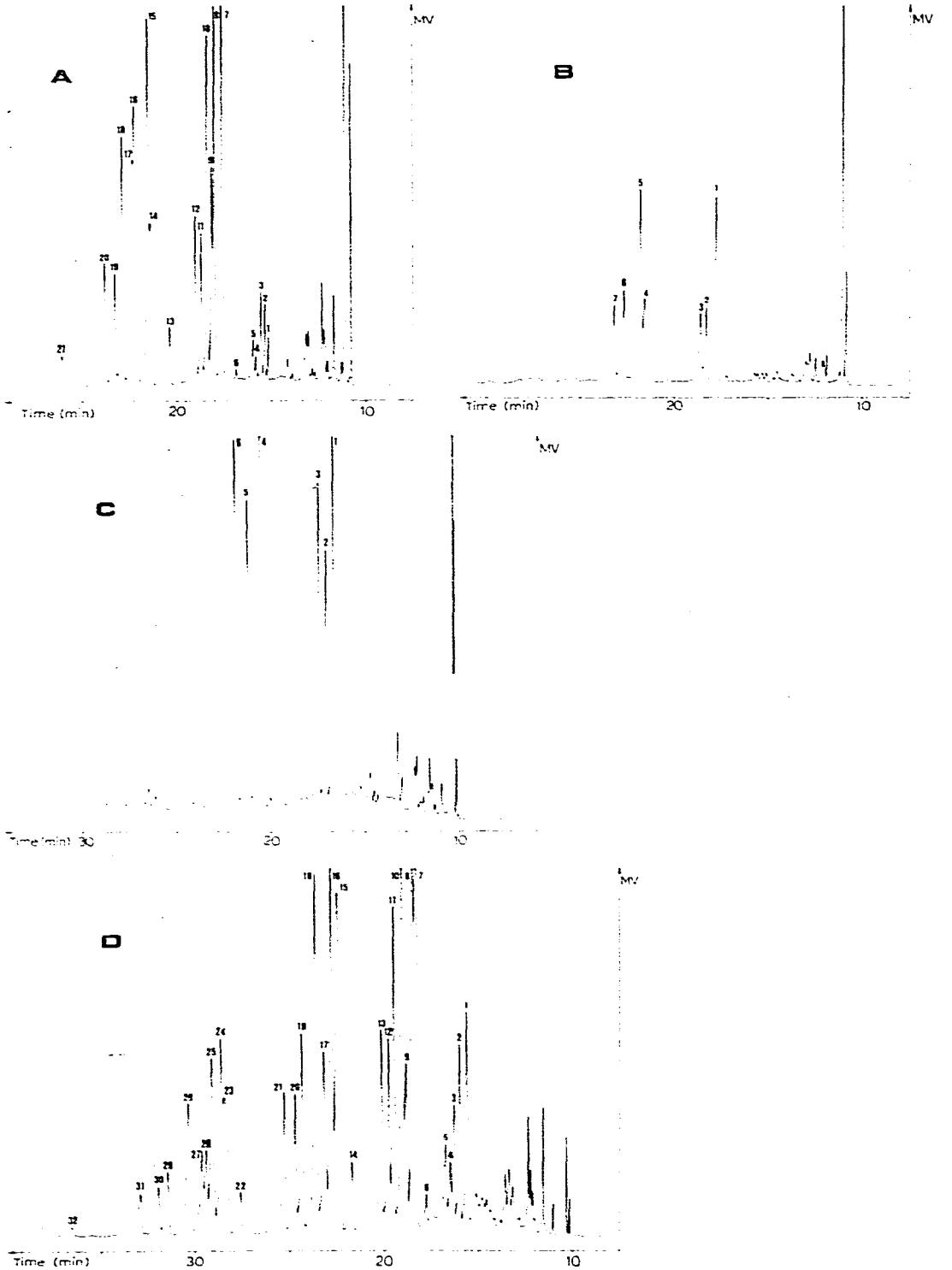


Fig. 3.

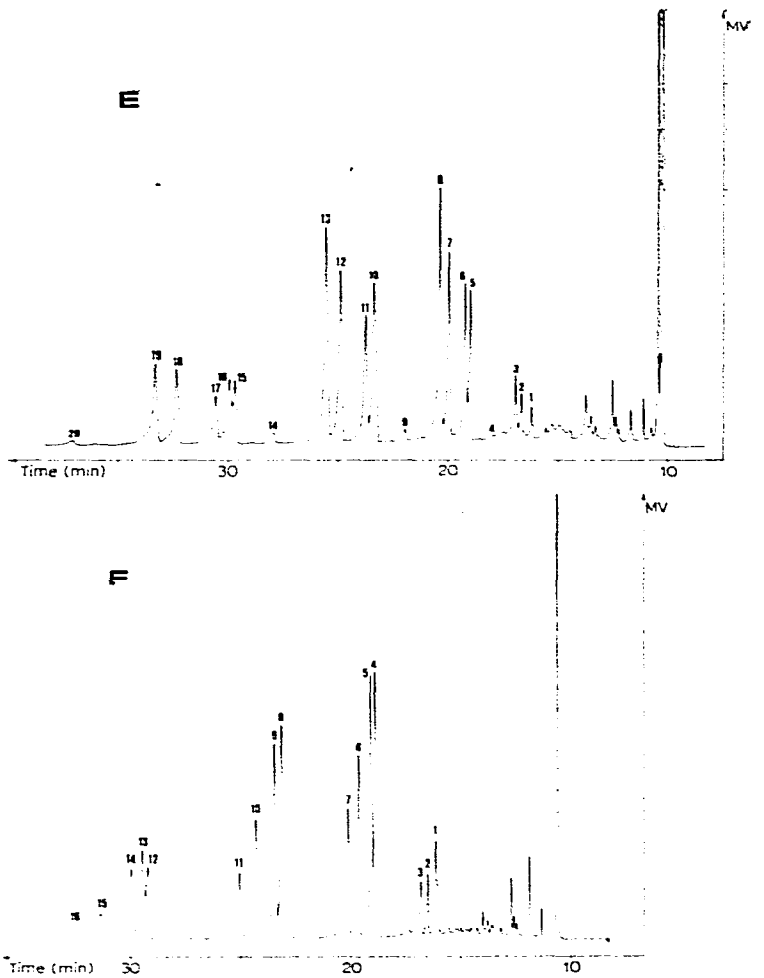


Fig. 3. Gas chromatograms of *n*-alkenes after chlorination. At the beginning of the chromatograms, peaks of the solvents and of impurities (aromatics, paraffins, unreacted alkenes) are present. Compounds are indicated as in the following example: C_8-*β-cis* = *vic*-dichloride derived from chlorination of *β-cis*-octene. Peaks in chromatogram A: chlorination of C_8–C_{10} *n*-alkenes, 1 = C_8-*δ-trans*; 2 = C_8-(*γ-trans* + *δ-cis*); 3 = C_8-*β-trans*; 4 = C_8-*γ-cis*; 5 = C_8-*β-cis*; 6 = C_8-*α*; 7 = C_9-*δ-trans*; 8 = C_9-*γ-trans*; 9 = C_9-*δ-cis*; 10 = C_9-*β-trans*; 11 = C_9-*γ-cis*; 12 = C_9-*β-cis*; 13 = C_9-*α*; 14 = C_{10}-*ε-trans*; 15 = C_{10}-*δ-trans*; 16 = C_{10}-(*γ-trans* + *ε-cis*); 17 = C_{10}-*δ-cis*; 18 = C_{10}-*β-trans*; 19 = C_{10}-*γ-cis*; 20 = C_{10}-*β-cis*; 21 = C_{10}-*α*. Peaks in chromatogram B: chlorination of *cis*-(C_8–C_{10}) *n*-alkenes, 1 = C_9-*δ*; 2 = C_9-*γ*; 3 = C_9-*β*; 4 = C_{10}-*ε*; 5 = C_{10}-*δ*; 6 = C_{10}-*γ*; 7 = C_{10}-*β*. C_8 and C_{11} present in low concentration. Peaks in chromatogram C: chlorination of *trans*-(C_8–C_{10}) *n*-alkenes, 1 = C_9-*δ*; 2 = C_9-*γ*; 3 = C_9-*β*; 4 = C_{10}-(*δ* + *ε*); 5 = C_{10}-*γ*; 6 = C_{10}-*β*. C_8 and C_{11} present in low concentration. Peaks in chromatogram D: chlorination of C_{10}–C_{13} *n*-alkenes, 1 = C_{10}-(*δ* + *ε*)-*trans*; 2 = C_{10}-(*δ-cis* + *ε-cis* + *γ-trans*); 3 = C_{10}-*β-trans*; 4 = C_{10}-*γ-cis*; 5 = C_{10}-*β-cis*; 6 = C_{10}-*α*; 7 = C_{11}-*ε-trans*; 8 = C_{11}-*δ-trans*; 9 = C_{11}- *ε-cis*; 10 = C_{11}-(*γ-trans* + *δ-cis*); 11 = C_{11}-*β-trans*; 12 = C_{11}-*γ-cis*; 13 = C_{11}-*β-cis*; 14 = C_{11}-*α*; 15 = C_{12}-(*ζ-trans* + *ε-trans*); 16 = C_{12}-*δ-trans*; 17 = C_{12}-(*ζ-cis* + *ε-cis*); 18 = C_{12}-(*γ-trans* + *δ-cis*); 19 = C_{12}-*β-trans*; 20 = C_{12}-*γ-cis*; 21 = C_{12}-*β-cis*; 22 = C_{12}-*α*; 23 = C_{13}-*ζ-trans*; 24 = C_{13}-*ε-trans*; 25 = C_{13}-*δ-trans*; 26 = C_{13}-*ζ-cis*; 27 = C_{13}-*ε-cis*; 28 = C_{13}-(*δ-cis* + *γ-trans*); 29 = C_{13}-(*β-trans*); 30 = C_{13}-*γ-cis*; 31 = C_{13}-*β-cis*; 32 = C_{13}-*α*. Peaks in chromatogram E: chlorination of *cis*-(C_{10}–C_{13}) *n*-alkenes, 1 = C_{10}-(*ε* + *δ*); 2 = C_{10}-*γ*; 3 = C_{10}-*β*; 4 = C_{10}-*α*; 5 = C_{11}-*ε*; 6 = C_{11}-*δ*; 7 = C_{11}-*γ*; 8 = C_{11}-*β*; 9 = C_{11}-*α*; 10 = C_{12}-(*ζ* + *ε*); 11 = C_{12}-*δ*; 13 = C_{12}-*γ*; 13 = C_{12}-*β*; 14 = C_{12}-*α*; 15 = C_{13}-*ζ*; 16 = C_{13}-*ε*; 17 = C_{13}-*δ*; 18 = C_{13}-*γ*; 19 = C_{13}-*β*; 20 = C_{13}-*α*. Peaks in chromatogram F: chlorination of *trans*-(C_{10}–C_{13}) *n*-alkenes: 1 = C_{10}-(*ε* + *δ*); 2 = C_{10}-*γ*; 3 = C_{10}-*β*; 4 = C_{11}-*ε*; 5 = C_{11}-*δ*; 6 = C_{11}-*γ*; 7 = C_{11}-*β*; 8 = C_{12}-(*ζ* + *ε*); 9 = C_{12}-*δ*; 10 = C_{12}-*γ*; 11 = C_{12}-*β*; 12 = C_{13}-*ζ*; 13 = C_{13}-*ε*; 14 = C_{13}-*δ*; 15 = C_{13}-*γ*; 16 = C_{13}-*β*. Chromatograms A–C and D–F were obtained under the same instrumental conditions by isothermal elution: oven temperature, 160° and 180° respectively. Peaks of the solvents and impurities are present at the beginning of the chromatograms.


MV
A
Time (min)
MV
B
Time min

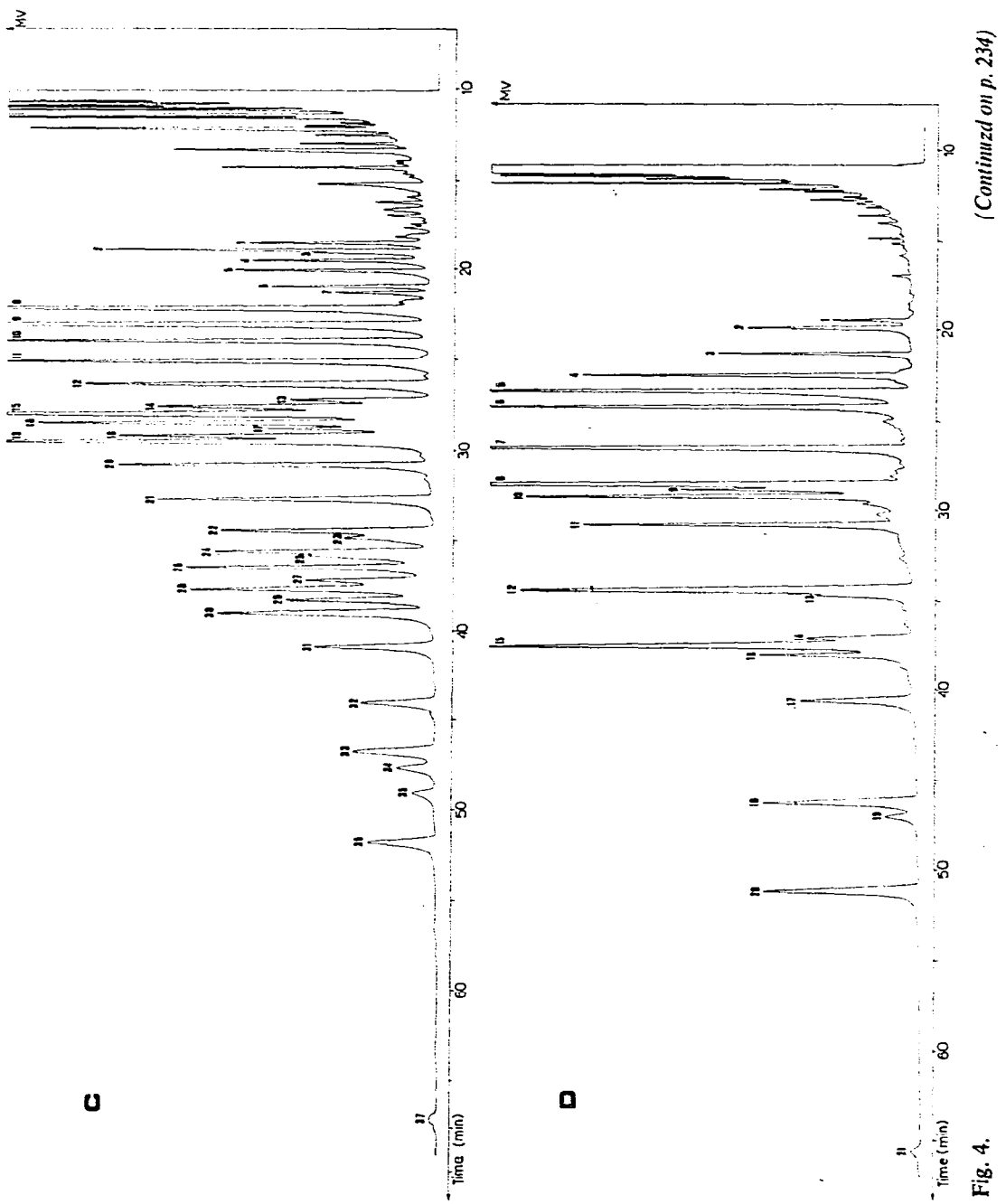


Fig. 4.

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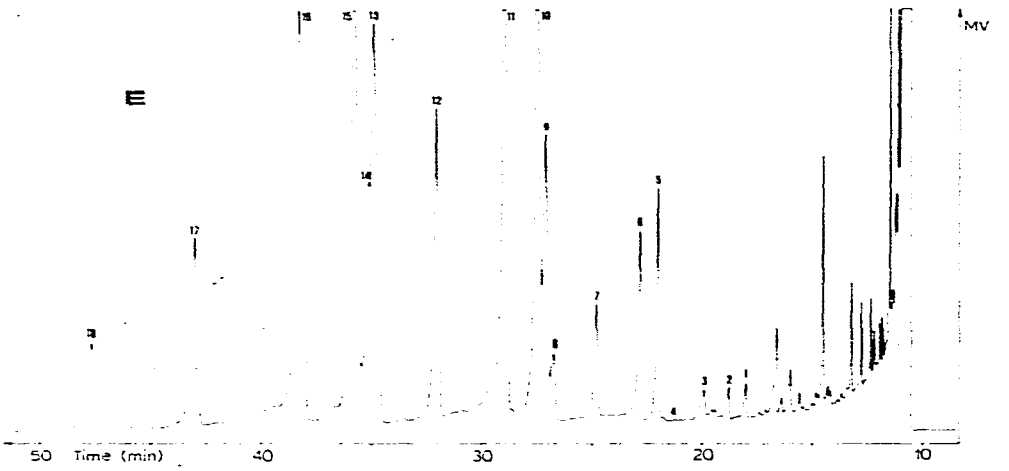

Fig. 4. Gas chromatograms of the silylated *vic*-diols obtained by oxidation of *n*-alkenes with osmium tetroxide. Compounds are indicated as in the following example: C_9-*β-trans* = silylated vicinal diol obtained by oxidation of *β-n*-octene with osmium tetroxide. Peaks in chromatogram A: oxidation of (C_8–C_{10}) *n*-alkenes, 1 = C_8-*δ-trans*; 2 = C_8-*δ-cis*; 3 = C_8-*γ-trans*; 4 = C_8-*γ-cis*; 5 = C_8-*β-trans*; 6 = C_8-*β-cis*; 7 = C_9-*δ-trans*; 8 = C_9-*δ-cis*; 9 = C_9-*γ-trans*; 10 = C_8-*α*; 11 = C_9-*γ-cis*; 12 = C_9-*β-trans*; between peaks 12 and 13, keto-alcohols (see Fig. 5) are found; 13 = C_9-*β-cis*; 14 = C_{10}-*ε-trans*; 15 = C_{10}-*ε-cis*; 16 = C_{10}-*δ-trans*; 17 = C_{10}-*δ-cis*; 18 = C_{10}-*γ-trans*; 19 = C_{10}-*γ-cis*; 20 = C_9-*α*; 21 = C_{10}-*β-trans*; 22 = C_{10}-*β-cis*; 23 = C_{10}-*α*. Peaks in chromatogram B: oxidation of *trans*-(C_8–C_{10}) *n*-alkenes with osmium tetroxide, 1 = C_8-*β*; 2 = sil-C_9-*γ*-keto-alcohol; 3 = C_9-*δ*; 4 = C_9-*δ-cis*; 5 = C_9-*γ*; 6 = C_9-*β*; 7 = sil-C_{10}-*δ*-keto-alcohol; 8 = C_{10}-*ε*; 9 = C_{10}-*δ*; 10 = sil-C_{10}-*β*-keto-alcohol; 11 = sil-C_{10}-*β*-keto-alcohol; 12 = C_{10}-*γ*; 13 = C_{10}-*β*. Peaks in chromatogram C: oxidation of (C_{10}–C_{13}) *n*-alkenes with osmium tetroxide, 1 = C_{10}-*ε-trans*; 2 = C_{10}-*ε-cis*; 3 = C_{10}-*δ-trans*; 4 = C_{10}-*δ-cis*; 5 = C_{10}-*γ-trans*; 6 = C_{10}-*γ-cis*; 7 = C_{10}-*β-trans*; 8 = C_{11}-*ε-trans*; shoulder of peak 8 towards peak 9 of C_{10}-*β-cis*; 9 = C_{11}-*ε-cis*; 10 = C_{11}-*δ-cis*; 11 = C_{11}-*γ-trans*; 12 = C_{11}-*γ-cis*; 13 = C_{11}-*β-trans*; 14 = C_{12}-*ζ-trans*; 15 = C_{12}-*ε-trans*; 16 = C_{11}-*β-cis*; 17 = C_{12}-*ζ-cis*; 18 = C_{12}-*ε-cis*; 19 = C_{12}-*δ-trans*; 20 = C_{12}-*δ-cis*; 21 = C_{12}-*γ-trans*; 22 = C_{12}-*γ-cis*; 23 = C_{11}-*α*; 24 = C_{13}-*ζ-trans*; 25 = C_{12}-*β-trans*; 26 = C_{13}-*ε-trans*; 27 = C_{13}-*ζ-cis*; 28 = C_{12}-*β-cis*; 29 = C_{13}-*ε-cis*; 30 = C_{13}-*δ-trans*; 31 = C_{13}-*δ-cis*; 32 = C_{13}-*γ-trans*; 33 = C_{13}-*γ-cis*; 34 = C_{12}-*α*; 35 = C_{13}-*β-trans*; 36 = C_{13}-*β-cis*; 37 = C_{13}-*α*. Peaks in chromatogram D: oxidation of *cis*-(C_{10}–C_{13}) *n*-alkenes with osmium tetroxide, 1 = C_{10}-*ε*; 2 = C_{10}-*δ*; 3 = C_{10}-*γ*; 4 = C_{10}-*β*; 5 = C_{11}-*ε*; 6 = C_{11}-*δ*; 7 = C_{11}-*γ* + C_{10}-*α*; 8 = C_{11}-*β*; 9 = C_{12}-*ζ*; 10 = C_{12}-*ε*; 11 = C_{12}-*δ*; 12 = C_{12}-*γ*; 13 = C_{11}-*α*; 14 = C_{13}-*ζ*; 15 = C_{12}-*β*; 16 = C_{13}-*ε*; 17 = C_{13}-*δ*; 18 = C_{13}-*γ*; 19 = C_{12}-*α*; 20 = C_{13}-*β*; 21 = C_{13}-*α*. Peaks in chromatogram E: oxidation of trans-(C_{10}–C_{13}) *n*-alkenes with osmium tetroxide, 1 = C_{10}-*ε*; 2 = C_{10}-*δ*; 3 = C_{10}-*γ*; 4 4 = C_{14}-*β*; 5 = C_{11}-*ε*; 6 = C_{11}-*δ*; 7 = C_{11}-*γ*; 8 = C_{11}-*β*; 9 = C_{12}-*ζ*; 10 = C_{12}-*ε*; 11 = C_{12}-*δ*; 12 = C_{12}-*γ*; 13 = C_{13}-*ζ*; 14 = C_{12}-*β*; 15 = C_{13}-*ε*; 16 = C_{13}-*δ*; 17 = C_{13}-*γ*; 18 = C_{13}-*β*. Chromatograms A, B and C–E were obtained under the same instrumental conditions by isothermal elution: oven temperature, 135° and 170° respectively. Impurities, unreacted alkenes, solvents and a small amount of degradation products are present at the beginning of the chromatograms.

The oxidation with hydrogen peroxide greatly increases the number of components to be determined because of the formation of keto alcohols[7] (positive reaction with dinitrophenylhydrazine, band at 1700 cm^{-1} in the IR spectrum, and mass spectra) and vicinal diols. The number of compounds to be evaluated is almost doubled. Therefore, component separations by GC become increasingly difficult as the molecular weight and complexity of the *n*-alkene mixture is increased. A typical gas chromatogram of a C_8–C_{10} fraction and the order of elution are shown in Fig. 5. Silylated keto alcohols (see formula (1)) have lower retention times than the cor-

TABLE V

RETENTION TIMES (IN ARBITRARY UNITS) OF SILYLATED DIOLS FROM C_8–C_{13} *n*-MONOALKENES

Position	*Carbon number*					
	8	*9*	*10*	*11*	*12*	*13*
α	1518	2514	4092	5721	8670	13064
β-cis	1164	1740	2887	4229	6391	9610
β-trans	1122	1608	2627	3947	5968	8999
γ-cis	1068	1542	2487	3748	5639	8482
γ-trans	990	1404	2269	3466	5228	7848
δ-cis	972	1344	2129	3195	4781	7143
δ-trans	924	1242	2013	2996	4488	6696
ε-cis			1963	2996	4394	6532
ε-trans			1851	2796	4112	6109
ζ-cis					4300	6297
ζ-trans					4030	5897

responding diols. In a C_8–C_{10} fraction the average total amount of keto alcohols was found to be 59.2% (w/w). The retention times of the diol and keto alcohol C_8–C_{10} mixture are given in Table VI.

TABLE VI

RETENTION TIMES OF SILYLATED C_8–C_{10} DIOLS AND KETO ALCOHOLS

A = a keto group in the internal position and a silyl group in the external position; B = the opposite situation; AB = equivalent positions. Retention times are referred to the same chromatogram and expressed in arbitrary units.

Position	*Carbon number*		
	8	*9*	*10*
Diols			
α		2320	3866
β-cis		1633	2655
β-trans	1002	—	2450
γ-cis	914	1446	2320
γ-trans	828	1310	2110
δ-cis		1260	1979
δ-trans		1159	1874
ε-cis			1823
ε-trans			1720
Keto alcohols			
β A	728	1220	2048
β B	684	1139	1901
γ A	651	1079	1796
γ B	626	1026	1698
δ A	595	970	1593
δ B + *ε* AB		941	1534

Fig. 5. Oxidation of C_8–C_{10} *n*-alkenes with hydrogen peroxide. The most abundant products of the oxidation are *vic*-diols and keto alcohols (see eqn. 1): sil-*vic*-diols are indicated as in Fig. 4, keto alcohols as in Table VI; *e.g.*, C_8-β_A = silyl ether of the C_8-keto alcohol in which substitution occurs at β (the silyl group is in the external position, B for internal and AB for equivalent positions). Peaks: 1 = C_8-δ_{AB}; 2 = C_8-γ_B; 3 = C_9-γ_A; 4 = C_8-β_B; 5 = C_8-β_A; 6 = C_8-*γ-cis*; 7 = C_8-*β-trans*; 8 = C_9-δ_B; 9 = C_9-δ_A; 10 = C_8-*β-cis*; 11 = C_9-γ_B; 12 = C_9-γ_A; 13 = C_9-β_B; 14 = C_9-*δ-trans*; 15 = C_9-β_A; 16 = C_9-*δ-cis*; 17 = C_9-*γ-trans*; 18 = C_8-*α*; 19 = C_9-*γ-cis*; 20 = (C_{10}-ε_{AB}) + (C_9-*β-trans*) + (C_{10}-δ_B); 21 = C_{10}-δ_A; 22 = C_9-*β-cis*; 23 = C_{10}-γ_B; 24 = C_{10}-*ε-trans*; 25 = C_{10}-γ_A; 26 = C_{10}-*ε-cis*; 27 = C_{10}-*δ-trans*; 28 = C_{10}-β_B; 29 = C_{10}-*δ-cis*; 30 = C_{10}-β_A; 31 = C_{10}-*γ-trans*; 32 = C_{10}-*γ-cis*; 33 = C_9-*α*; 34 = C_{10}-*β-trans*; 35 = C_{10}-*β-cis*; 36 = C_{10}-*α*.

Mass spectrometry

Identifications of the oxidation product of the alkenes with OsO_4 and H_2O_2 were carried out by GC–MS using the same capillary column as employed for the GC analyses. Bis(trimethylsilyl) derivatives of vicinal diols which differ only in the position of substitution on the linear hydrocarbon chain have similar MS behaviour. Molecular ions are not present, and the fragmentation pattern is much influenced by the charge delocalization induced by the ether groups. Mass spectra of typical silanized keto alcohols and diols are shown in Fig. 6. As observed by other workers[4], the original double-bond position is indicated by two intense fragments of similar intensity each containing a silyl group formed by bond cleavage ($[R–CH=O–Si(CH_3)_3]^+$). The weak ions at *m/e* 103, *m/e* 117 and *m/e* 73 are attributed respectively to the fragments $[CH_2=O–Si(CH_3)_3]^+$, $[CH_3–CH=O–Si(CH_3)_3]^+$ and $[(CH_3)_3Si]^+$. The peak derived from loss of 15 *m/e* $^+$ units from the molecular ion is of low intensity. The mass spectra of the keto alcohols show the characteristic base peak of the ion $R'–CH=O^+Si(CH_3)_3$

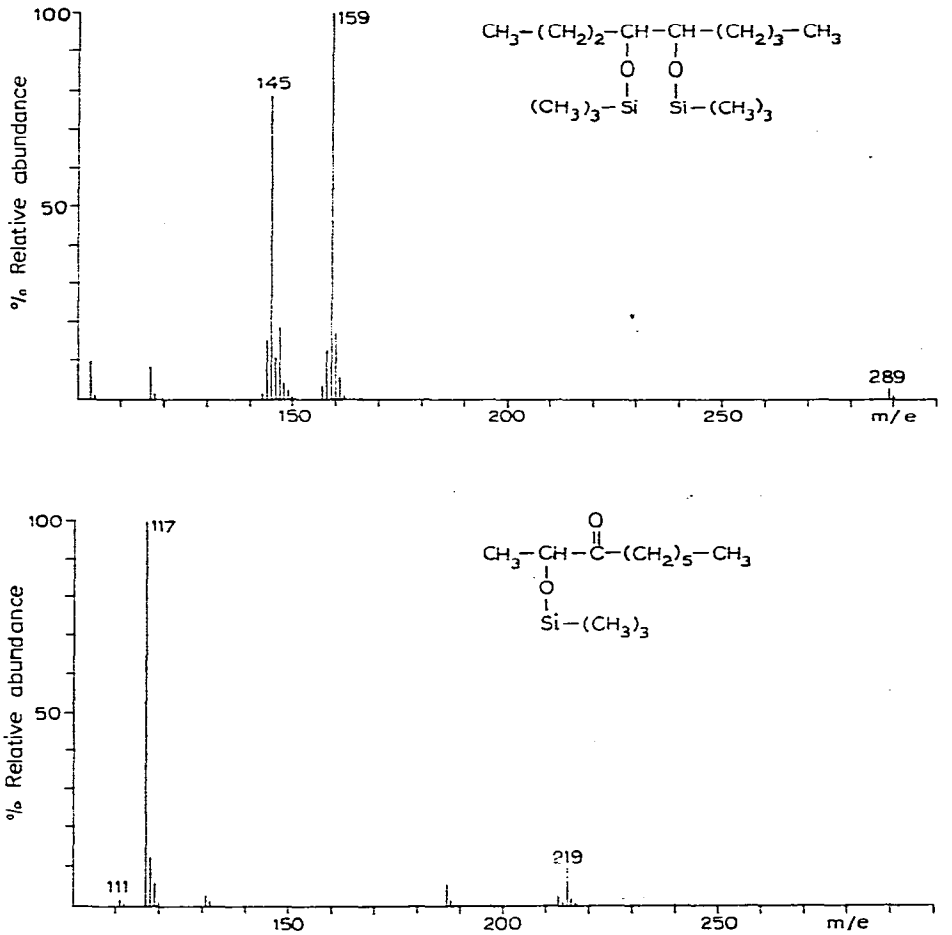

Fig. 6. Typical mass spectra of the silyl ethers of *vic*-diols and keto alcohols obtained by oxidation of *n*-alkenes.

which indicates the position of the substitution. The parent ion M^+ is not present; however, $M^+ - 15$ is usually of medium intensity. Weak peaks derived from loss of the R unit in the form of $C_nH_{2n-1}^+$ aside the silyl group with abstraction of one proton, but only for long chain R is observed. The fragmentation of the keto group yields unsaturated RCO^+ ions.

Finally, the molecular weight and the point of substitution of the original double bond can be conveniently deduced by observation of the mass value of the $M^+ - 15$ and $R-CH=O^+Si(CH_3)_3$ peaks.

Quantitations

The methods of chlorination and oxidation with OsO_4 are in principle suitable for the determination of the relative abundance of the positional and geometrical isomers. On the contrary, the oxidation with H_2O_2 leads partially to the formation of keto alcohols in which the original geometry of the alkenes is not retained, but only the position of substitution, and determinations of the *cis*- and *trans*-isomers cannot be carried out.

On the basis of the gas chromatograms of the alkene derivatives, it has been shown that the average yields are >97% for chlorination and >93% for oxidation reactions*. The conditions for the chlorination reaction were adjusted in order to obtain complete transformation of pure α-alkenes used for standardization. In fact, it has been observed that some chlorination conditions influence the selectivity of transformation of the α-*n*-alkenes with respect to the internal alkenes. No particular selectivity of the reaction appears to exist for the *cis*- or the *trans*-isomers. The chlorine content in the chlorination product was found to be very near the theoretical value.

In the oxidations with OsO_4, even when the structure is retained, the determination of the amount of *trans*- and *cis*-compounds is of low precision and lower concentration for *trans*-compounds is generally found (~20% relative error). The data obtained for the analysis of a sample and for its *cis*- and *trans*-fractions are consistent (see also Fig. 4). This behaviour has not been investigated further, but seems to have little influence on the determination of the positional isomers and of the carbon number distribution (see Table VII).

The direct injection into the gas chromatograph of the alkene mixtures and the *cis*- and *trans*-fractions allows a quantitative determination of the geometrical isomers by using as internal standard the β-*cis*- or the β-*trans*-isomers (see Figs. 1 and 2 and Table IX).

It must be pointed out that the principal scope of the described analytical methods is the determination of the internal double-bond positions in the original alkene mixtures. In fact the total number of *cis*-, *trans*- and α-isomers can easily be determined by IR spectroscopy by measuring the intensity of the adsorption bands at 960 cm^{-1} (*trans*-) and 910 cm^{-1} (α). A comparison between results obtained by the use of different methods of analysis for the same samples is shown in Table VII. In Table VIII the results are expressed in normalized form for each carbon number, and

* The "technical" Olex product contains, typically, 95% *n*-alkenes plus branched alkenes (0.5%), alkanes (1.2%), dienes (2.3%) and aromatics (1.0%). Some of these impurities are found at the beginning of the chromatograms.

TABLE VII

CONTENT OF POSITIONAL ISOMERS DETERMINED BY DIFFERENT METHODS
Results in % (v/v).

Sample	*Carbon number*	*Position*	*Method*			
			Oxidation with Cl_2	*Oxidation with OsO_4*	*Oxidation with H_2O_2*	*GC of alkenes**
C_8–C_{10}	8	α	0.4	0.4	0.3	
		β	2.8	2.0	2.6	3.3
		γ	2.5	1.5	2.4	
		δ		1.5	0.9	
		Total	5.7	5.4	6.2	7.3
	9	α	2.6	3.4	3.0	
		β	13.0	14.4	~15.5**	12.4
		γ	12.7	13.6	12.7	
		δ	15.7	16.5	15.7	
		Total	44.0	47.9	(~46.9)	47.4
	10	α	2.7	2.5	3.0	
		β	11.9	11.4	11.9	10.5
		γ	9.5	10.7	11.1	
		δ	26.2	8.2	(~20.9)**	
		ε		13.9		
		Total	50.3	46.7	(~46.9)	45.3
C_{10}–C_{13}	10	α	0.9	0.4		
		β	3.6	3.3		2.7
		γ	1.8	2.5		
		δ	2.8	1.9		
		ε	2.3	2.7		
		Total	11.4	10.8		10.7
	11	α	1.1	1.8		
		β	8.6	7.1		8.3
		γ	8.2	8.4		
		δ	9.0	11.1		
		ε	8.9	8.9		
		Total	35.8	37.3		32.7
	12	α	0.9	0.8		
		β	4.9	5.4		5.4
		γ	7.2	6.2		
		δ	7.7	9.0		
		ε	18.2	8.5		
		?		4.6		
		Total	38.9	34.5		35.4
	13	α	0.4	0.3		
		β	2.2	2.3		2.3
		γ	3.7	2.6		
		δ	4.1	4.4		
		ε	5.3	4.4		
		?	4.4	3.8		
		Total	20.1	17.8		21.2

* Content of β position only is reported.

** Overlap of C_9-β and C_{10}-(δ + ε) is observed. The sum of these positions is 36.4; individual values are obtained from the results of analysis for single carbon-number cuts.

TABLE VIII

CONTENT OF POSITIONAL ISOMERS (VALUES NORMALIZED FOR EACH CARBON NUMBER)

C_8 was not included because of its low concentration in the analyzed samples.

Carbon number	*Position*	*Method*					
		Oxidation with Cl_2		*Oxidation with OsO_4*	*Oxidation with H_2O_2*	*GC of alkenes*	
9	α	5.9		7.1	6.4		
	β *cis*	29.5	11.4	30.1	(33.0)*	26.2	10.9
	β *trans*		18.1				15.3
	γ	28.9		28.4	27.1		
	δ	35.7		34.4	33.5		
10**	α	5.4		5.4	6.3		
	β *cis*	23.7	8.3	24.4	25.4	23.1	9.2
	β *trans*		15.4				13.9
	γ	18.9		22.9	23.7		
	δ	52.0		17.6	(44.6)*		
	ε			29.7			
11	α	3.1		4.8	—		
	β *cis*	24.0	12.6	19.0	—	25.4	9.5
	β *trans*		11.4				15.9
	γ	22.9		22.5	—		
	δ	25.1		29.8	—		
	ε	24.9		23.9	—		
12	α	2.7		2.3	—		
	β *cis*	15.0	7.0	15.7	—	15.3	7.7
	β *trans*		8.0				7.9
	γ	22.0		18.0	—		
	δ	23.5		26.1	—		
	ε	36.8		24.6	—		
	ζ			13.3	—		
13	α	2.0		1.7	—		
	β *cis*	10.9	5.5	12.9	—	10.8	5.6
	β *trans*		5.4				5.2
	γ	18.4		14.6	—		
	δ	20.4		24.7	—		
	ε	26.4		24.8	—		
	ζ	21.9		21.3	—		

* See footnote** in Table VII concerning the overlap of single positions.

** Calculated by analysis of the C_8–C_{10} sample.

Table IX compares results obtained for α and geometrical isomers by the use of the described methods with those obtained by IR spectroscopy. In Table X a comparison is made of results for a C_{10}–C_{13} *cis*-fraction.

The repeatability for each method is shown in Table XI. The calculated relative mean error between results found for each positional isomer (*cis* + *trans*) using different methods is *ca.* $\pm 6.6\%$ (maximum error 21.5%), assuming as true the mean value of the results obtained by the different methods.

TABLE IX

CONTENT OF α AND GEOMETRICAL ISOMERS IN SAMPLES OF *n*-ALKENES

Method	C_8–C_{10}		C_{10}–C_{13}	
	Total α	*Total trans*	*Total* α	*Total trans*
Oxidation with Cl_2	5.7	61.5*	3.3	64.3*
Oxidation with OsO_4	6.3	— **	3.3	— **
Oxidation with H_2O_2	6.3	—	—	—
GC of alkenes	—	not determined	—	70.3
IR spectroscopy	5.8	69.4	3.5	69.7

* Approximate value because of peak overlap.
** See text.

TABLE X

USE OF DIFFERENT METHODS FOR THE CALCULATION OF THE *cis*-FRACTION OF A C_{10}–C_{13} ALKENE MIXTURE AND COMPARISON OF THE RESULTS

Normalized values for each carbon number are in parentheses.

Carbon number	*Position*	*Method*		
		Oxidation with Cl_2	*Oxidation with* OsO_4	*GC of alkenes*
10	β	3.1 (44.3)	4.7 (48.0)	3.5 (42.2)
	γ	1.9 (27.1)	2.3 (23.5)	2.7 (32.5)
	δ	1.4 (20.0)	1.9 (19.4)	2.1 (25.3)
	ε	0.6 (8.6)	0.9 (9.1)	
	Total	7.0	9.8	8.3
11	β	11.8 (35.8)	12.3 (31.3)	11.8 (30.9)
	γ	7.7 (23.3)	9.4 (23.9)	11.8 (30.9)
	δ	6.9 (20.9)	6.7 (17.0)	6.2 (16.2)
	ε	6.6 (20.0)	10.9 (27.7)	8.4 (22.0)
	Total	33.0	39.3	38.2
12	β	11.8 (32.7)	10.4 (30.4)	10.4 (29.6)
	γ	8.6 (23.8)	9.2 (26.8)	9.3 (26.4)
	δ	6.9 (19.1)	5.5 (16.0)	6.3 (17.9)
	ε	8.8 (24.4)	6.0 (17.5)	9.2 (26.1)
	ζ		3.2 (9.3)	
	Total	36.1	34.3	35.2
13	β	6.3 (26.4)	5.0 (30.1)	4.6 (25.1)
	γ	5.9 (24.7)	4.0 (24.1)	4.0 (21.9)
	δ	3.9 (16.3)	2.6 (15.7)	2.7 (14.8)
	ε	7.8 (32.6)	2.6 (15.7)	7.0 (38.2)
	ζ		2.4 (14.5)	
	Total	23.9	16.6	18.3

TABLE XI

REPEATABILITY OF THE METHODS

The variability of the results for each component is characterized by a mean value of the standard deviation calculated for each component.

Oxidation method	*Standard deviation*
Cl_2	0.328
OsO_4	0.367
H_2O_2	0.305

CONCLUSIONS

Some observations can be made about the application of the described methods. When making a choice between the derivatization reactions, the time of analysis and ease of execution must be considered. Another important factor is the quality of result which is required.

The evaluation of the β-isomers in complex C_8–C_{13} *n*-alkene mixtures can easily be made by direct GC analysis of the underivatized samples; the content of α- and geometrical isomers is rapidly determined by IR spectroscopy without sample transformation. Chlorine oxidation requires a short reaction time and few derivatization steps. This method provides the identification of *ca.* 80% of the components in the examined carbon-number range. A correct evaluation of the relative amounts of *trans*- and *cis*-isomers is obtained.

The method of oxidation with OsO_4 provides a separation of *ca.* 95% of the components and the results obtained for the positional isomers are similar to those obtained with the other described methods. However, the evaluation of the geometrical isomers leads to incorrect results.

The effectiveness of the separations is enhanced if the sample is previously separated into the *cis*- and *trans*-fractions by column chromatography, or if the alkene mixture is separated by preparative GC in fractions of single carbon number.

Oxidation with H_2O_2 is not generally suitable for these determinations. The interpretation of the results is difficult, the separations are inconvenient and samples of high molecular weight cannot be analyzed. Moreover, the formation of the keto alcohols almost doubles the complexity of the mixture. This method has been described in order to show that these components can be present in small amounts even when the sample is oxidized only with OsO_4.

The lack of available standards over the entire C_8–C_{13} range does not allow the evaluation of the accuracy of each method. However, from an examination of all the results we can conclude: (a) the total amount of α-isomers as determined by IR spectroscopy is in good agreement with that found by the described methods (see Table IX); (b) β-*cis* and β-*trans*-isomers, and possibly some internal isomers, are well separated in the gas chromatograms of the underivatized alkenes, their amounts can easily be calculated (these data are considered to be highly reliable since no derivatizations are required) and agreement with the other methods is found (see Table VIII); (c) by the use of the same procedure, the analyses of a *cis*-fraction can be compared. (In this instance, GLC of the alkenes can effect a separation of some internal isomers and the comparison is therefore more appropriate, see Table X.)

Finally, the agreement between quantitative results obtained by using the different methods (chlorination, oxidation with OsO_4 and GC of alkenes) is sufficient but not optimal. It must be noted that the complexity of the mixtures analyzed produces a high number of degrees of freedom. Therefore, when comparing the quantitative results, unsystematic discrepancies may be found. This is attributed more to the derivatization reactions than to the GC analysis conditions. Nevertheless, from Table VIII, it can be seen that substantial agreement is obtained. The repeatability of the methods is sufficient to provide a tool for the systematic quality control of alkene samples. In addition, the structural informations obtained (supported by IR and GC–MS analyses) may be useful in determining the transformation steps of alkene mixtures in the production of oxo alcohols, alkylbenzenes, alkylphenols and other substances of wide use in the petrochemical industries.

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