IDENTIFICATION OF n-HEPTA- AND n-OCTADIENES BY HIGH-RESOLUTION GAS CHROMATOGRAPHY USING STRUCTURE–RETENTION CORRELATIONS AND MASS SPECTROMETRY

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SUMMARY

Concentrated dehydrogenation product mixtures of *n*-heptane and *n*-octane were separated on squalane capillary columns. All *n*-heptadienes and *n*-octadienes were identified, with the exception of those with cumulated double bonds.

Because of a lack of standards, retention data and mass spectra, the problem of identification was solved by using structure–retention correlations derived from available retention data for alkenes. The identification was then confirmed by using the ageing effect of a squalane column, which gives rise to characteristic changes in selectivity for different classes of unsaturated hydrocarbons. Confirmation was also made by determination of dI/dT values and by gas chromatography–mass spectrometry. The anomalous behaviour of compounds containing C=C–C–C–C structural elements, as noted before for alkenes, alkynes and alkylbenzenes, was found to occur also with *n*-alkadienes.

INTRODUCTION

Catalytic dehydrogenation of *n*-alkanes yields mainly all the possible isomers of *n*-alkenes and characteristic alkylbenzenes with a corresponding number of carbon atoms[1]. Small amounts of other products are formed[2–4], of which *n*-alkadienes are the most interesting from theoretical and practical standpoints.

In a previous study[4] the identification of *n*-hexadienes in mixtures of dehydrogenation products of *n*-hexane was discussed. The identification was based on a comparison of measured and tabulated retention indices on non-polar (squalane) and polar (Arneel SD) stationary phases. The identification of *n*-hexadienes was confirmed by gas chromatography–mass spectrometry (GC–MS). Identification of dienes with more than six carbon atoms is more complicated because of the increasing number of isomers. Only a few retention data and mass spectra of *n*-hepta- and *n*-octadienes

are available in the literature. Of the 17 possible isomers of n-heptadiene, retention data for only five isomers with isolated 1,6-, 1,5- and 1,4- double bonds[5-9] are known. Mass spectra are available of 1,6- and 2,4-heptadienes[10]. Although the number of isomers is considerably larger for n-octadienes, more reference data are available in this instance. Of the 26 possible isomers, retention data for 19 n-octadienes, mostly in ref. 9, are known. The mass spectra of 1,7-, 1,6-, 1,3- and 2,6-octadienes are available[10].

Because of a lack of standards, retention data and mass spectra for many dienes, we undertook to solve the problem of identification by using structure–retention correlations derived from available retention data for structurally corresponding alkenes and by GC–MS.

EXPERIMENTAL

In dehydrogenation product mixtures, prepared according to a procedure described earlier[11], dienes are present in only small amounts (totalling a few tenths of 1%). Therefore, the dienes were concentrated by adsorption column chromatography on silica gel by the FIA method.

Gas chromatography was carried out with a Carlo Erba GI 450 instrument, equiped with a flame-ionization detector (FID). For the separations, two squalane capillary columns were used. The first column (SQ-1) was made of stainless steel, of length 200 m and I.D. 0.25 mm. This column was operated at temperatures between 30° and 100°. Nitrogen was used as the carrier gas at an inlet pressure of 0.25 MPa. The average carrier gas velocity was 8.8 cm/sec. The theoretical and effective plate numbers were 372,000 and 245,000, respectively, at 70° for cis-2,cis-4-octadiene with a capacity ratio of 4.3. The qualitative reproducibility was 0.2 index units (i.u.). This column was used over 9 years at temperatures up to 130° and showed characteristic changes in retention indices, particularly for unsaturated hydrocarbons (ageing effect). The second squalane column (SQ-2) was a freshly coated glass capillary column of length 70 m and I.D. 0.25 mm. The theoretical and effective plate numbers were 170,000 and 105,000, respectively, for cis-2,cis-4-octadiene with a capacity ratio of 3.7 at 70°. Nitrogen was used as the carrier gas at an inlet pressure of 0.07 MPa. The average carrier gas velocity was 8.3 cm/sec. The concentrated samples were introduced in amounts of less than 1 μl via a splitter with a splitting ratio 1:100.

Electron-impact (EI) mass spectra were obtained on a Finnigan 4000 quadrupole instrument, coupled directly to the SQ-1 column described above. Helium was used as the carrier gas at an inlet pressure of 0.2 MPa. The separations were carried out at 70°. Samples were injected on to the column via a splitter with a splitting ratio 1:200. Mass spectra were obtained using an ionizing energy of 70 eV and an electron current of 0.20 mA. Mass spectra were recorded at a speed of 1 sec per scan.

RESULTS AND DISCUSSION

The mixtures of concentrated dehydrogenation products of n-heptane and n-octane were separated at different temperatures on both squalane columns. Representative chromatograms of these mixtures obtained with the first column (SQ-1) are
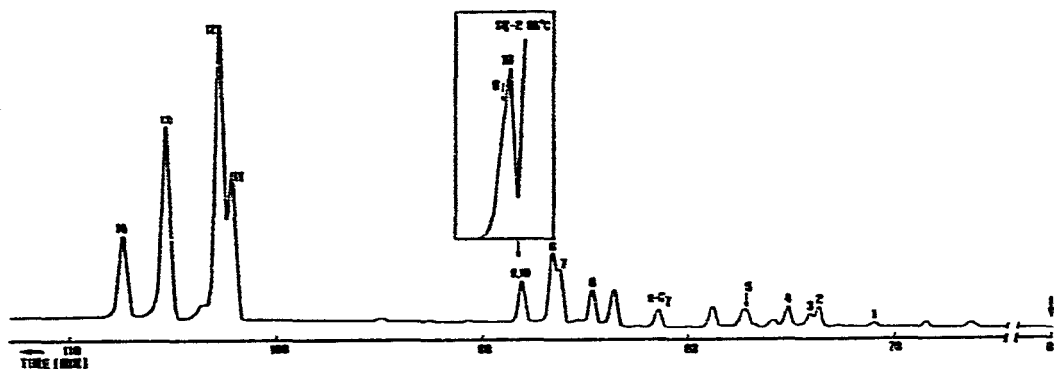
Fig. 1. Chromatogram of the concentrated dehydrogenation product mixture of *n*-heptane on the SQ-1 column at 70°. For identification of *n*-heptadienes, see Table I.

presented in Figs. 1 and 2. Calculated and measured retention indices of the *n*-hepta-dienes and *n*-octadienes studied are given for both columns in Table I.

The identification of *n*-dienes was effected by comparison of measured and published retention indices, using calculated structural increments for both squalane columns (H^{SQ}), the ageing effect of the SQ-1 column, dI/dT values and GC–MS. Identification of conjugated *trans*-isomers was verified by reaction of the sample with maleic anhydride.

Comparison of measured and literature retention data

Comparison with retention indices of *n*-heptadienes from the literature shows systematic differences up to 3.7 i.u. for 1,*cis*-5-heptadiene[5,9]. For *n*-octadienes differences up to 1.2 i.u. are found for *cis*-2,*cis*-6-octadiene[6,7]. These differences can be ascribed mainly to polarity differences of the squalane columns and the compounds
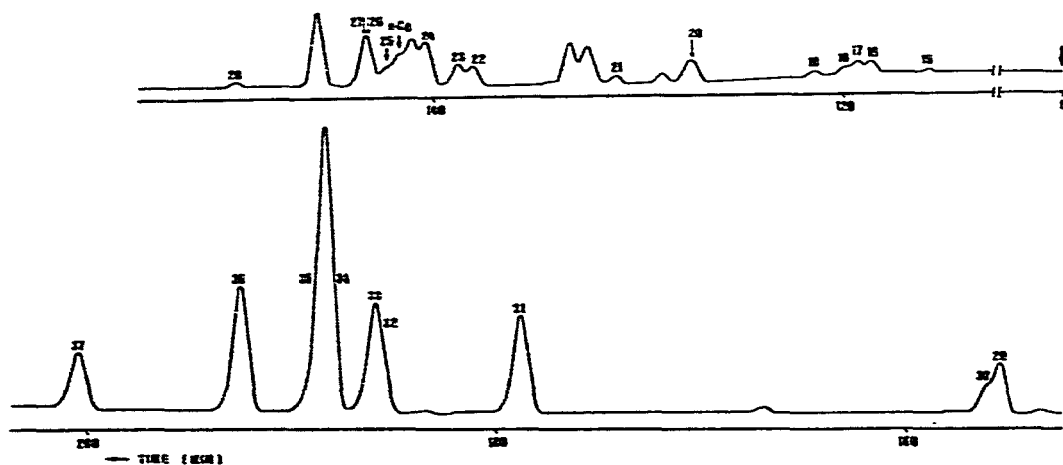

Fig. 2. Chromatogram of the concentrated dehydrogenation product mixture of *n*-octane on the SQ-1 column at 70°. For identification of *n*-octadienes, see Table I.

TABLE I

CALCULATED AND MEASURED VALUES OF RETENTION INDICES AND THEIR
TEMPERATURE INCREMENTS FOR n-HEPTADIENES AND n-OCTADIENES ON SQ-1
AND SQ-2 COLUMNS

Peak No.	Compound	SQ-1			SQ-2		
		I_{calc}^{70}	I_{meas}^{70}	dI/dT	I_{calc}^{70}	I_{meas}^{70}	dI/dT
1	1,6-Heptadiene	668.8	668.3	0.070	665.2	664.8	0.070
2	1,trans-4-	673.0	677.2	−0.005	670.1	674.0	−0.005
3	1,cis-4-	677.1	678.6	0.045	674.0	675.1	0.045
4	1,trans-5-	684.3	681.9	0.013	681.3	678.8	0.015
5	1,cis-5-	690.0	688.1	0.055	686.6	684.5	0.055
6	trans-2,trans-5-	700.0	708.3	−0.020	697.4	705.1	−0.020
7	trans-2,cis-5-	705.7	712.3	0.005	702.7	708.8	0.005
8	1,trans-3-	673.0	713.1	0.035	670.1	708.8	0.035
9	cis-2,cis-5-	711.4	716.4	0.060	708.0	712.5	0.060
10	1,cis-3-	677.1	716.5	0.050	674.0	712.1	0.055
11	trans-2,cis-4-	692.8	745.4	0.020	690.1	740.7	0.029
12	trans-2,trans-4-	688.7	746.5	0.040	686.4	742.2	0.040
13	cis-2,trans-4-	694.4	751.1	0.020	691.5	746.5	0.030
14	cis-2,cis-4-	698.5	754.6	0.035	695.4	749.9	0.040
15	1,7-Octadiene	767.0	767.8	0.060	763.6	764.2	0.060
16	1,trans-4-	768.6	771.7	0.020	766.0	768.7	0.020
17	1,trans-5-	773.1	772.6	0.022	770.5	769.6	0.020
18	1,cis-5-	774.1	773.5	0.053	770.7	770.0	0.050
19	1,cis-4-	772.5	775.5	0.055	769.5	772.4	0.055
20	1,trans-6-	782.9	783.3	0.037	779.9	779.8	0.035
21	1,cis-6-	787.7	787.9	0.070	784.2	784.0	0.060
22	trans-2,trans-6-	798.8	796.0	−0.018	796.2	793.4	−0.010
23	trans-2,cis-5-	790.0	796.9	0.020	787.7	793.4	0.020
24	trans-2,trans-5-	789.0	798.6	−0.030	786.8	795.5	−0.030
25	cis-2,cis-5-	794.8	800.6	0.060	791.3	796.7	0.060
26	trans-2,cis-6-	803.6	801.6	0.022	800.5	798.1	0.020
27	cis-2,trans-5-	793.8	801.7	0.015	791.1	798.3	0.020
28	cis-2,cis-6-	808.4	808.4	0.068	804.8	804.5	0.070
29	1,trans-3-	773.1	815.4	0.050	770.5	811.1	0.050
30	1,cis-3-	774.1	816.0	0.065	770.7	810.9	0.065
31	trans-3,cis-5-	780.2	835.9	0.013	777.6	831.1	0.025
32	cis-3,cis-5-	781.2	841.4	0.030	777.8	836.6	0.035
33	trans-2,cis-4-	788.4	841.4	0.030	785.8	836.6	0.040
34	trans-2,trans-4-	784.5	843.3	0.040	782.3	838.7	0.055
35	trans-3,trans-5-	779.2	843.3	0.040	777.4	838.7	0.055
36	cis-2,trans-4-	789.3	846.3	0.023	786.6	841.4	0.040
37	cis-2,cis-4-	793.2	851.9	0.045	790.1	846.9	0.060

to be identified. Because of its relative significance for dienes this effect was taken
into account in the identification by comparison of measured and published data.

Structural increment, H^{SQ}

From retention indices of structurally corresponding n-heptenes and n-octenes
measured on the SQ-1 and SQ-2 columns and the resulting structural increments

$(H^{SQ})^5$, retention indices of *n*-heptadienes and *n*-octadienes were calculated as shown in the following equations:

$$I^{SQ}_{n-alkene} - I^{SQ}_{n-alkane} = H^{SQ}_{n-alkene}$$

$$H^{SQ}_{n-alkene\ (a)} + H^{SQ}_{n-alkene\ (b)} = H^{SQ}_{n-diene}$$

$$H^{SQ}_{n-diene} + I^{SQ}_{n-alkane} = I^{SQ}_{n-diene}\ (= I^{SQ}_{calc}\ \text{in Table I})$$

For dienes with isolated functional groups Schomburg and Dielmann[8] reported good agreement between the experimental data and the values calculated on the basis of incremental contributions to the H^{SQ} values. This agreement diminishes with decreasing distance between the functional groups. The conjugation causes a considerable and characteristic increase in H^{SQ} (30–40 i.u.)[5] compared with the corresponding alkenes (conjugation effect). In a previous study on the analysis of *n*-hexadienes[4] we also observed that the agreement between experimental and calculated retention indices depends on the position of and the distance between the double bonds in the molecules of isomers. This agreement decreases in the order 1,5-, 1,4-, 2,3-, 1,2-, 1,3-, 2,4-hexadienes. The largest difference was observed for *cis*-2,*cis*-4-hexadiene (53 i.u.).
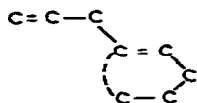
Values of retention indices of *n*-heptadienes and octadienes on SQ-1 and SQ-2 columns calculated from retention indices of the corresponding alkenes also measured on these columns are given in Table I. The differences between the calculated retention indices appear to be 3 i.u. on average and are smaller for *trans*- and higher for *cis*-diene isomers. They are caused by the different polarities of the two squalane columns.

For the SQ-2 column the calculated and experimental data are in good agreement for dienes with more isolated double bonds. For 2,5-hepta- and -octadienes the differences between the experimental and calculated values are larger (6 i.u. on average). The interactions of the double bonds result in an increased retention index for these types of dienes. As expected, this effect is considerably lower for 1,4-isomers: for example, 1.5 i.u. for 1,*cis*-4-heptadiene, although the "distance" between the double bonds is the same as for 2,5-dienes. Compared with 1,*cis*-4-heptadiene the difference for 1,*trans*-4-heptadiene is significantly higher (4 i.u.). Considering the fact that the retention index of the latter is calculated from H^{SQ} values of 1-heptene and *trans*-3-heptene, this can be explained.

In a previous paper[11] it was shown that in a graph of structural increments of *n*-alkenes (H^{SQ}) *versus* the number of carbon atoms for the homologous series of *trans*-3-alkenes, some anomaly was observed for *trans*-3-heptene. A similar anomaly was observed for *trans*-4-octene in the homologous series of *trans*-4-alkenes. Their retention indices are lower than expected from this relationship. A corresponding effect was also observed for their boiling points. This effect was ascribed to a particular stereo-specific ring arrangement of the *trans*-3-heptene molecule. This arrangement is not possible for 1,*trans*-4-heptadiene. The discrepancy between the calculated and measured retention indices for 1,*trans*-4-heptadiene is in good agreement with the observed value of the anomaly effect with *trans*-3-heptene (about 3 i.u.).

For 1,*trans*-4-octadiene, however, the retention index is calculated from structur-

al increments (H^{SQ}) of 1-octene and anomalous *trans*-4-octene. In this instance there is no significant discrepancy between the calculated and measured data, because the stereospecific arrangement responsible for the anomalous behaviour is also present in the 1,*trans*-4-octadiene molecule:

C = C — C
         ⟍
          C = C
           ⟍   ⟍
            ⁞   C
             C — C ⟋

For conjugated dienes the difference between measured and calulated retention indices is considerably larger (39–42 i.u. for 1,3-hepta- and -octadienes, 52–59 i.u. for 2,4-hepta- and -octadienes and 55–63 i.u. for 3,5-octadienes). For 2,4-heptadienes the largest differences were found for *trans*-2,*trans*-4- and *cis*-2, *trans*-4-isomers. Both were calculated from H^{SQ} values of anomalous *trans*-3-heptene. While this particular stereospecific ring arrangement is not possible for either of these heptadienes, in this instance also the difference between calculated and measured retention data is higher. For conjugated octadienes the H^{SQ} values increased in the order, 1,3-, 2,4-, 3,5-isomers. Thus the effect of conjugation in 3,5- is greater than that in 2,4-isomers.

We could prove that the structural increment, H^{SQ}, for the individual types of dienes decreases characteristically with the number of carbon atoms in the molecule in a manner similar to that for *n*-alkenes[11].

To permit the identification of the dienes in the dehydrogenation product mixture the approach described before was used to predict the elution order and retention indices of the compounds for which no reference data or standards are available. The corrections for effects due to stereospecific arrangements, as discussed above, were taken into account in this preliminary identification.

Ageing effect of squalane column

The measured retention indices on the two squalane columns (Table I) are different owing to a difference in polarity caused by ageing of the SQ-1 column. This ageing effect enables one to distinguish between different classes of hydrocarbons (ΔI values are on average 2 i.u. for alkenes, 4 i.u. for *n*-dienes and 10 i.u. for alkylbenzenes). It is even possible to discriminate between different types of compounds within a class of hydrocarbons. For instance, the ΔI values of *cis-n*-alkenes are higher than those of *trans*-isomers. For dienes with isolated double bonds mean ΔI values
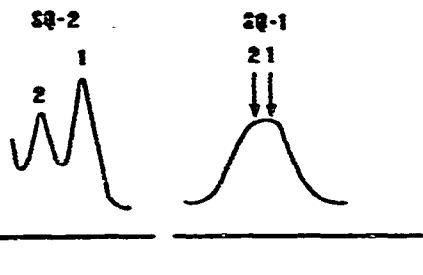

Fig. 3. Separation of 1,*trans*-6-octadiene (1) and 1-octene (2) on SQ-1 and SQ-2 columns at 70°.

of 3 i.u. are observed, while ΔI values for conjugated dienes are significantly higher (5 i.u.). The effect of ageing on the separation of the compounds in the mixture being analysed is exemplified in Fig. 3 with 1-octene and 1,*trans*-6-octadiene, and in Fig. 4 with ethylbenzene and 2,4-octadienes. In this way the ageing of the column can be used either to confirm a preliminary identification or for group identification of the compounds to be analysed.
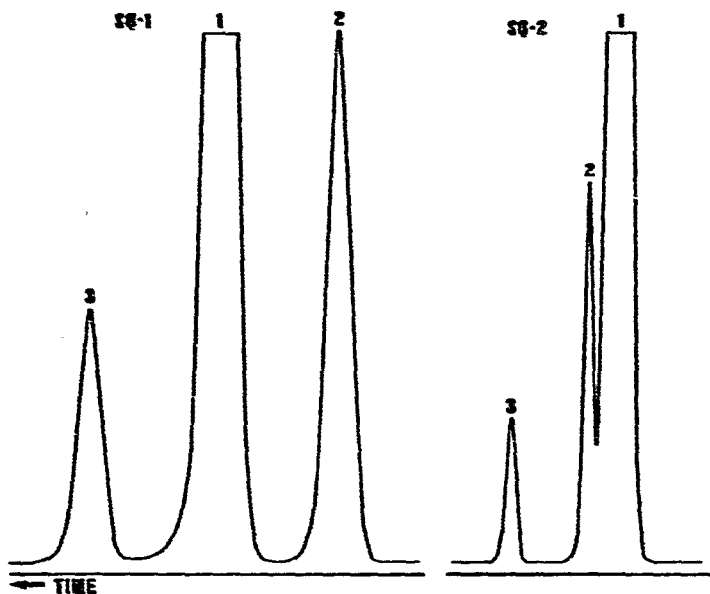

Fig. 4. Separation of ethylbenzene (1) from *cis*-2,*trans*-4-octadiene (2) and *cis*-2,*cis*-4-octadiene (3) on SQ-1 and SQ-2 columns at 70°.

Temperature increments, dI/dT

In addition to *n*-dienes, cycloalkenes and alkynes are also present in the dehydrogenation product mixtures. The similarity of their mass spectra is a serious complication for structural elucidation by GC–MS.

The dI/dT values[8,11,12], which are significantly higher for cycloalkenes than for dienes, can be used to distinguish between these classes of compounds. This is illustrated as an example in Fig. 5. At 50° the cycloalkene (1-ethylcyclopentene) is eluted before the diene (*cis*-2,*trans*-4-heptadiene) on the SQ-1 column. At 70° these compounds are not separated, while at 80° the elution order is reversed. Because dI/dT values of *n*-hepta- and *n*-octadienes (ranging from —0.02 to 0.07 i.u./°C) are of the same order as those of *n*-hepta- and *n*-octaalkynes (—0.07 to 0.00), these classes cannot be discriminated in this way. However, *n*-alkynes with an internal triple bond (2-, 3-, 4-) have characteristically higher negative values of dI/dT[13,14]. Data for non-linear hepta- and octaalkynes are not available.

In a previous paper[11] we discussed the relationship between dI/dT values and geometry and the position of the double bond for *n*-alkenes on squalane as the stationary phase. It was shown that the existing correlations can be used to optimize the separation and can be applied for the identification of isomers. For dienes,
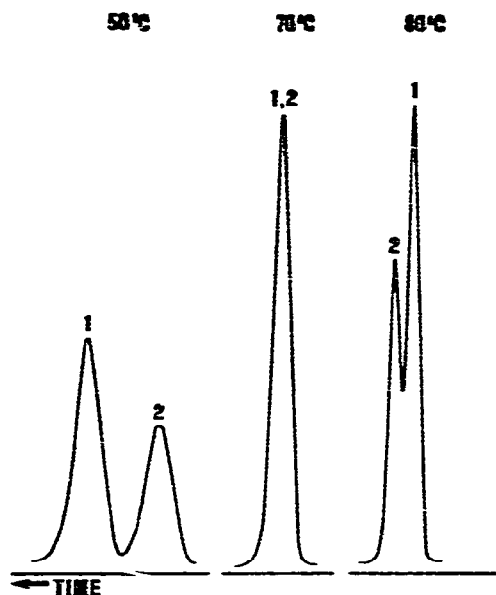
Fig. 5. Separation of cis-2,trans-4-heptadiene (1) and 1-ethylcyclopentene (2) on the SQ-1 column at 50°, 70° and 80°.

however, this type of correlation is less evident. For isolated dienes the dI/dT values for cis-isomers are relatively high and larger than for the corresponding trans-isomers[9]. For conjugated dienes this phenomenon cannot be observed. They have relatively high dI/dT values. For cis–trans alkenes, dI/dT depends on the symmetry of the molecule. The asymmetric cis-isomers have larger dI/dT values than the corresponding symmetrical trans-isomers. Probably the effect of symmetry of the molecule on dI/dT plays a similar role for the conjugated dienes. For instance, the dI/dT values of 2,4-heptadienes increase in the order trans-2,cis-4-, cis-2,trans-4-, cis-2,cis-4-, trans-2,trans-4-isomers.

Reaction of n-dienes with maleic anhydride

Identification of 1,trans-3- and trans-2,trans-4-heptadienes was verified by reaction with crystalline maleic anhydride by heating for 30 min at 50°. As demonstrated in Fig. 6, only conjugated n-dienes in the trans-configuration take part in this reaction[15,16].

Mass spectra

While the chromatograms in Fig. 1 and 2 were obtained after repeated concentration of the dienes, GC–MS was carried out earlier on samples concentrated only once by adsorption column chromatography on silica gel. The mixtures subjected to GC–MS still contained alkenes in relatively high concentrations. Some dienes were coeluted with and hence obscured by these compounds.

As mentioned before, only a few reference spectra of n-dienes are available. It might be expected that alkynes, cycloalkenes and branched alkadienes will yield similar spectra. Moreover, as discussed below, the relationship between structure and
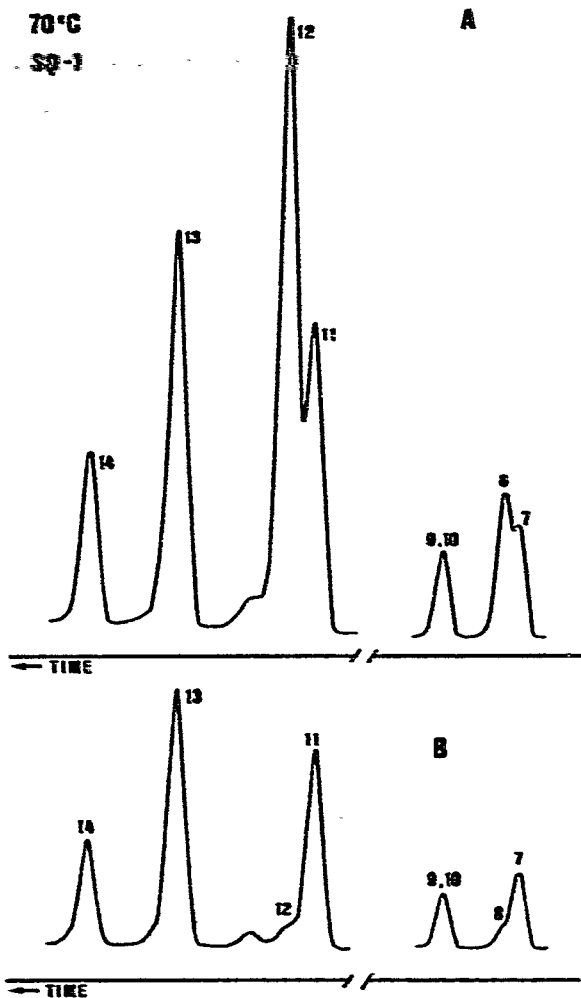
Fig. 6. Chromatogram of conjugated *n*-heptadienes on the SQ-1 column at 70°: (A) before reaction with maleic anhydride and (B) after this reaction.

mass spectra of dienes is not evident. Owing to these circumstances, mass spectrometry could not be used as a positive identification method. It was rather used as an elimination method, mainly based on molecular weight determinations, to distinguish dienes from alkenes and other hydrocarbons. The EI mass spectra of *n*-heptadienes and *n*-octadienes are summarized in Tables II and III, respectively.

From these tables the following conclusions can be drawn. Within the groups of *n*-heptadienes and *n*-octadienes (except for those with cumulated double bonds), all positional isomers yield different spectra and hence can be identified on this basis. The only exceptions are 2,4- and 3,5-octadienes, which give similar spectra that cannot be distinguished.

Cis,trans-isomers are difficult, if not impossible, to distinguish on the basis of their 70-eV EI mass spectra.

TABLE II

RELATIVE INTENSITIES (%) OF MAIN IONS (ABOVE m/e 50) IN THE EI MASS SPECTRA OF n-HEPTADIENES

m/e	Peak No. (Fig. 1)[*]								
	1[**]	2	3	4[***]	6	7[§]	8[§]	11/12	14[§§]
96	2	24	20	3	53	52	42	51	53
82	2	6	7	2	10	7	3	9	9
81	32	68	59	30	100	100	38	100	100
80	1	4	4	1	8	7	2	7	8
79	2	31	22	5	52	45	16	39	42
78	—	4	4	1	2	2	2	2	4
77	2	10	9	2	12	12	8	11	13
69	1	1	4	—	5	2	2	2	1
68	23	11	15	5	10	10	10	8	10
67	40	63	65	18	36	39	56	25	28
66	4	6	7	3	6	7	6	6	7
65	2	18	15	2	10	15	17	12	11
56	4	8	8	9	12	6	3	2	4
55	75	59	43	100	52	44	27	24	27
54	100	100	100	16	27	45	100	27	30
53	25	38	46	18	54	47	22	37	40
52	3	10	7	3	6	7	5	6	6
51	7	10	11	4	7	6	6	8	9

[*] For identification, see Table I.

[**] cf., Reference spectrum MSDC 4364[10].

[***] 1,cis-5-Heptadiene was obscured by trans-3-heptene.

[§] cis-2,cis-5- and 1,cis-3-heptadiene were not separated; spectra omitted.

[§§] trans-2,cis-4- and trans-2,trans-4-heptadiene were not separated. cis-2,trans-4-Heptadiene was eluted under ethylcyclopentene-1. A reference spectrum of 2,4-heptadiene was present in our unpublished file.

The stability of the molecular ions is roughly inversely proportional to the distance between the double bonds. Conjugated n-heptadienes (1,3- and 2,4-) and n-octadienes (2,4- and 3,5-) give abundant molecular ions (42–67%), whereas strongly isolated double bonds (1,5-, 1,6- and 1,7-) cause weak molecular ions (1–8%).

Some fragmentation pathways can be formulated by the concept of charge localization, followed by β-fissions (allylic cleavages) or McLafferty rearrangements. Simple β-cleavages give rise to the base peaks in the spectra of, e.g., 1,5-heptadiene and 2,6-octadiene (m/e 55), and 2,4-heptadiene and 3,5-octadiene (m/e 81). McLafferty rearrangements explain the base peaks in the spectra of, e.g., 1,6-heptadiene (m/e 54) and 1,6-octadiene (m/e 68):

m/e 110 m/e 68
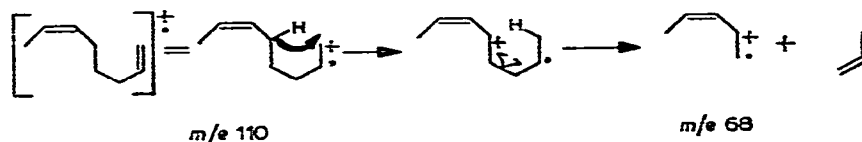
In most instances, however, the interpretation of the spectra is more complicated. For instance, the genesis of the base peaks at m/e 54 from 1,3-heptadiene or 1,7-

TABLE III

RELATIVE INTENSITIES (%) OF MAIN IONS (ABOVE *m/e* 50) IN THE EI MASS SPECTRA OF *n*-OCTADIENES

m/e Peak No. (Fig. 2)*	15**	16***	19	17/18¹	21¹¹	22¹¹¹	27¹¹¹	28¹¹¹	23†	29††	30††	31	32/33†††	34/35ᵃ	36	37
110	1	6	6	8	2	5	9	13	30	34	24	67	58	52	58	46
95	11	12	9	7	12	11	13	31	23	5	5	44	22	26	17	16
82	40	14	15	4	15	3	4	5	6	5	7	9	9	8	8	7
81	32	40	24	32	48	20	33	60	77	27	27	100	100	100	100	100
80	1	3	4	3	2	2	4	2	7	2	3	11	8	8	6	8
79	3	12	18	17	15	5	11	11	32	15	14	43	46	39	49	50
78	1	2	4	—	—	1	1	2	2	1	2	6	4	4	2	3
77	—	12	6	8	3	3	5	6	13	7	8	21	18	16	18	12
69	18	100	60	28	40	2	3	3	5	8	8	10	7	7	7	8
68	36	22	24	27	100	6	18	14	63	26	23	88	75	73	81	84
67	85	53	39	100	76	8	20	25	64	86	100	93	57	60	51	58
66	6	9	6	10	6	1	2	3	6	8	8	7	11	8	10	9
65	4	—	8	9	2	2	3	7	8	17	13	15	10	11	12	9
56	8	—	25	—	3	11	11	11	8	7	5	6	3	3	3	2
55	35	18	100	40	70	100	100	100	100	21	19	60	27	32	26	30
54	100	21	33	36	80	10	11	11	13	100	88	13	11	9	11	11
53	22	21	27	28	38	10	17	18	38	16	13	49	48	27	48	52
52	3	—	9	4	2	—	1	3	9	8	3	6	5	7	6	6
51	5	—	2	10	5	1	3	5	—	3	5	8	5	6	7	6

* For identification, see Table I.

** *cf.*, Reference spectra API 236m and ASTM 1897[10].

*** See text.

¹ 1,*cis*-5- and 1,*trans*-5-octadiene were not separated.

¹¹ *cf.*, Reference spectrum ASTM 1896[10]. 1,*trans*-6-octadiene was obscured by 1-octene.

¹¹¹ *cf.*, Reference spectrum ASTM 1895[10], which matches best with the spectrum of *trans*-2, *trans*-6-octadiene. *trans*-2,*cis*-6- and *cis*-2,*trans*-5-octadiene were poorly separated. However, the former appears to be the main compound (compare with the spectra of *trans*-2,*trans*-6- and *cis*-2, *cis*-6-octadiene on the one hand, and *trans*-2,*cis*-5-octadiene on the other).

† *trans*-2,*trans*-5- and *cis*-2,*cis*-5-octadiene were obscured by *trans*-2-octene; the latter also by *n*-octane. *cis*-2,*trans*-5-octadiene was obscured by *trans*-2,*cis*-6-octadiene (see ¹¹¹).

†† A reference spectrum of 1,3-octadiene was present in our unpublished file.

††† *cis*-3,*cis*-5- and *trans*-2,*cis*-4-octadiene were not separated, but have similar spectra (compare with spectra of peak numbers 31 *vs.* 36 and 37).

ᵃ *trans*-3,*trans*-5-octadiene was not separated from *trans*-2,*trans*-4-octadiene (see also †††).

octadiene through McLafferty rearrangements, or the loss of a methyl radical from 1,6-heptadiene (*m/e* 81, 32%) through β-fission, cannot be explained in this way. The formation of these ions must involve double bond migration, often to the conjugated position, followed by allylic cleavage or rearrangement reactions[17].

The mass spectrum of peak 16 (Fig. 2, Table III) needs further comment. Because this spectrum differs considerably from all other spectra in Table III, peak 16 was originally rejected as being an octadiene. However, there is reasonable proof that peak 16 represents 1,*trans*-4-octadiene. The results of the FIA method, by which *n*-alkadienes are concentrated compared with *n*-alkenes and cycloalkenes, support this assignment. Moreover, other hydrocarbons with a molecular weight of 110 having I^{SO} values between 750 and 790 are not found in the literature.

If peak 16 is indeed properly assigned, it is tempting to relate its spectrum, which differs distinctly from the mass spectrum of 1,cis-4-octadiene, to its anomalous chromatographic behaviour. Keeping in mind the proposed stereospecific arrangement of 1,trans-4-octadiene, as a rationale for the observed chromatographic anomaly, one might tentatively postulate the rearrangement of its molecular ion to the allylcyclopentane ion under 70-eV EI conditions. This intermediate (which cannot be formed in the case of 1,cis-4-octadiene) can easily fragment to produce the cyclopentyl ion, which is the base peak in the spectrum of peak 16:

m/e 69
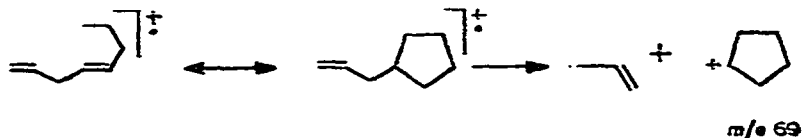
The spectrum of peak 16 indeed shows close similarities to the spectrum of allylcyclopentane (API 1988)[10]. (I_{70}^{SQ} for allylcyclopentane is unknown, but is expected to be above 800; for propylcyclopentane $I_{70}^{SQ} = 834$). Exciting as this speculation might be, several objections can be made. Firstly, the mass spectra of cis-2-hexene (API 406) and anomalous trans-2-hexene (API 99) are very similar and completely different from that of methylcyclopentane (API 117)[10]. Secondly, while the mass spectra of cis-3-heptene and cis-4-octene were not found in the literature, the spectra of anomalous trans-3-heptene (API 931) and trans-4-octene (API 129) are again completely different from those of ethylcyclopentane (API 184) and propylcyclopentane (API 190), respectively[10]. In conclusion, the best guess seems to be that peak 16 is actually composed of a mixture of 1,trans-4-octadiene and an unknown compound.

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