CHROM. 21 086

SEPARATION AND CHARACTERIZATION OF METHYLCYCLOPENTADIENE DIMERS BY GAS CHROMATOGRAPHY AND MOLECULAR SPECTROSCOPY

M. A. DÍEZ, F. J. FAÑANAS[a], C. G. BLANCO and J. BERMEJO*

Instituto Nacional del Carbón y sus Derivados "Francisco Pintado Fe", C.S.I.C., Ap. 73, 33080-Oviedo (Spain)

(First received July 6th, 1988; revised manuscript received November 4th, 1988)

SUMMARY

The number and dimeric nature of the components of a commercial mixture of methylcyclopentadiene dimers was established by capillary gas chromatography on different stationary phases and temperatures of 80 and 100°C. The mixture was later fractionated by preparative gas chromatography into fractions containing pure or major components. Some of the dimers are transformed into isomers with an exocyclic double bond. The assignment of structures was carried out on the basis of nuclear magnetic resonance spectroscopic data for the dimers and iso-dimers.

INTRODUCTION

Mixtures of methylcyclopentadiene isomers are frequently obtained by thermal cracking of petroleum and similar hydrocarbon fractions. When isomers were separated by gas chromatography (GC) it was found that the main components of industrial mixtures were the 1-methyl (I) and the 2-methyl (II) forms (Fig. 1). The 5-methyl isomer (III) was always present in very low concentration[1,2].

Diels-Alder reactions of methylcyclopentadienes can theoretically give rise to numerous adducts with *endo*- or *exo*-dicyclopentadiene skeletons, but it is generally accepted that adducts exist mainly in the *endo* form (IV) and arise from isomer I and II reacting as a diene and (or) dienophile[2].

Attempts to elucidate the structure of adducts present in commercial mixtures were made through dimerization of mixtures of I and II of known composition[2] as well as by desdimerization of fractions obtained by preparative GC[3]. However, while Musaev *et al.*[4] supposed hat the dienophile reacted through the double bond close to the methyl group, Franklin[5] and Zharov *et al.*[6] assumed that only the unsubstituted double bond was involved. Consequently, there are few reliable results.

When GC on columns packed with different stationary phases was used for the

---

[a] Present address: Departamento de Química Organometálica, Facultad de Química, Universidad de Oviedo, Oviedo, Spain.

TABLE I

CAPILLARY COLUMNS AND OPERATING CONDITIONS

| Parameter	Column					
	1^a	2^b	3^b	4^a	5^a	6^b
Stationary phase	Squalane	SE-54	OV-1701	UCON LB 550X	TXP	OV-215
Length (m)	45	25	25	50	46	25
Internal diameter (mm)	0.50	0.22	0.22	0.25	0.50	0.22
Carrier gas (nitrogen) flow-rate (ml min^{-1})	1.30	1.50	1.00	1.00	2.90	0.85
Splitting ratio	1:91	1:53	1:120	1:92	1:52	1:194
Detector and injector temperatures (°C)	170	170	170	170	170	170
McReynolds polarity	0	337	789	996	1500	1545
Number of theoretical plates	78 000	95 000	118 000	76 500	80 000	94 000

[a] Stainless steel.
[b] Fused silica.
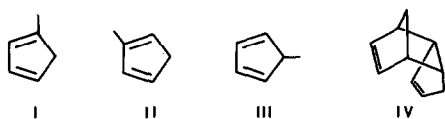
Fig. 1. 1-Methyl- (I), 2-methyl- (II) and 5-methyl-1,3-cyclopentadiene (III); *endo*-dicyclopentadiene (IV).

separation of the resulting adducts, it was clearly established that the dimer arising from I was the least retained while that from II had the highest retention time[2,5]. The same conclusion was made by Langer *et al.*[3] from a study by ^{1}H NMR spectroscopy of three fractions separated by preparative GC. Moreover, these authors assigned structures on the basis of the ^{1}H NMR spectra of the fractions, assuming that these were constituted by only one component. Nevertheless, they did not report either evidence in support of a such a supposition or the spectroscopic data on which the structural assignment was based.

The aim of this work was to further the knowledge of the structures of the dimers present in commercial mixtures. To this end, the number and dimeric nature of the components was first studied by capillary GC on six stationary phases of different polarities (McReynolds scale[7]). The mixture was later fractionated by preparative GC and the composition of the fractions and the structure of the main components was studied by capillary GC and NMR spectroscopy, respectively. The discovery of isomerization reactions involving some of the dimers was of estimable help in the structural assignment.

EXPERIMENTAL

The mixture of methylcyclopentadiene dimers used was supplied by Fluka (technical grade).

Analyses by capillary GC were carried out with Hewlett-Packard 5830A and Perkin-Elmer 8320 chromatographs equipped with flame ionization detection (FID). The capillary columns and operating conditions used are listed in Table I.

Preparative GC was performed on a Perkin-Elmer F21 chromatograph. The methylcyclopentadiene dimer mixture was fractionated using a series of three stainless-steel columns (1 m × 8 mm I.D.), packed with 10% silicone E-301-Chromosorb P N AW (60–80 mesh) with a nitrogen flow-rate of 160 ml min^{-1} and an oven temperature of 100°C.

A mixture with 78% of the isomer of dimer 7 (iso-dimer 7) was obtained by preparative GC from the commercial mixture isomerized by flowing hydrogen chloride into it. A series of three columns (0.90 m × 8 mm I.D.) packed witn 5% Bentone 34 and 5% diisodecyl phthalate on Chromosorb W DMCS (60–80 mesh) was used with a nitrogen flow-rate of 146 ml min^{-1} and an oven temperature of 95°C.

Infrared (IR) spectra were recorded on a Perkin-Elmer Infracord 137 instrument, from samples deposited on NaCl.

^{1}H NMR spectra of samples solved in CCl$_4$ were obtained on a Varian FT-80 (80 MHz) spectrometer, using tetrmethylsilane (TMS) as the internal standard. ^{13}C NMR spectra were recorded on a Varian FT-80 spectrometer; off-resonance decoupling experiments were also carried out.
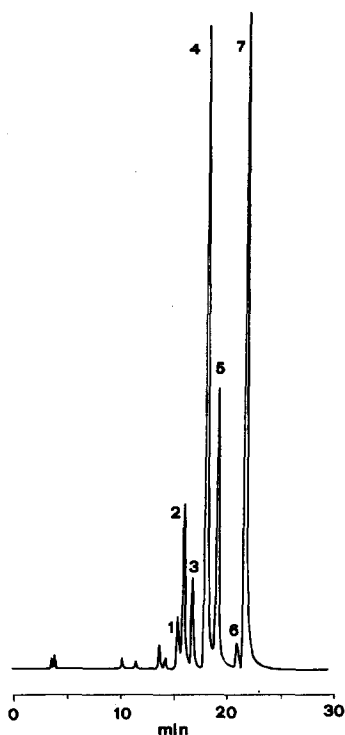
Fig. 2. Chromatogram of a commercial mixture of methylcyclopentadiene dimers on squalane at 100°C. The numbered peaks belong to dimeric compounds.

GC–mass spectrometry (MS) was performed on an Hewlett-Packard 5987 A instrument. Electron impact spectra were recorded at an ionization energy of 70 eV.

RESULTS AND DISCUSSION

Studies on the composition of complex mixtures are usually undertaken by capillary GC using several stationary phases of different chromatographic polarities and by changing the operating conditions. In this way the highest number of components can be detected.

In addition to the possibility of *endo* and *exo* isomers, mixtures of methyl-cyclopentadiene dimers can be constituted by numerous isomers some of which differ only in the position of one of the methyl groups, including the positions close to the same double bond. For this reason six capillary columns with stationary phases whose polarities range from 0 to 1550 on the McReynolds scale were used for the separation of the dimers at 80 and 100°C (Table I).

The retention times relative to *endo*-dicyclopentadiene of the main components of the mixture (peaks 1–7 in Fig. 2) are shown in Table II. These data reveal that the six stationary phases resolved the mixture into the same seven peaks. Respective peaks have almost identical areas in all chromatograms and the seven components have the

TABLE II

RELATIVE RETENTIONS OF THE METHYLCYCLOPENTADIENE DIMERS IN THE COM-
MERCIAL MIXTURE ON DIFFERENT STATIONARY PHASES AT 100°C

For chromatographic conditions see Table I.

Peak No.	Squalane	SE-54	OV-1701	UCON LB 550X	OV-215	TXP
	1.00[a]	1.00	1.00	1.00	1.00	1.00
	(9.99)[b]	(7.41)	(5.039)	(5.93)	(4.08)	(8.77)
1	1.49	1.41	1.28	1.27	1.21	1.24
2	1.54	1.44	1.31	1.31	1.24	1.28
3	1.61	1.48	1.35	1.38	1.28	1.37
4	1.74	1.64	1.48	1.47	1.35	1.47
5	1.84	1.66	1.52	1.60	1.40	1.60
6	2.01	1.83	1.63	1.76	1.44	1.73
7	2.09	1.90	1.71	1.82	1.49	1.79

[a] Retention time relative to endo-dicyclopentadiene.
[b] Absolute retention time of endo-dicyclopentadiene.

same molecular weight [m/e 160 (M$^+$)]. Therefore, it can be stated that the commercial mixture consists of seven components of dimeric nature, of which the principal ones, peaks 2, 4, 5 and 7, were the subject of further study, assuming that they had the structure of endo-dicyclopentadiene.

The ^{1}H NMR spectrum of the commercial mixture shows signals at 6.0–5.7, 5.45 and 5.05 ppm typical of olefinic hydrogens in 1-methylnorbornene[8,9], 2-methyl-norbornene[8–10] and methylcyclopentene bound to cycloaliphatic structures[11,12], respectively. Other possible dimeric structures, such as those bearing methyl groups on carbon atoms which join rings of norbornene and cyclopentene (secondary bridge-head), are not present, at less in detectable concentrations. Therefore, it seems apparent that dienophiles mainly react by the unsubstituted double bond. The IR spectrum of the mixture shows only two small bands in the region of the C=C stretching vibration at 1660 and 1630 cm^{-1} compatible with the above mentioned structures.

Dimer 7 was isolated by preparative GC. The most significant feature of its ^{1}H NMR spectrum (Fig. 3a) is the absence of signals at 6.0–5.7 ppm which rules out structures like 1-methylnorbornene. The 2-methylnorbornene ring of dimer 7 obviously results from a Diels-Alder reaction in which isomer II reacts as a diene. Its highest retention time and concentration in the commercial mixture (Fig. 2) shows, on the basis of previous work[2,3,6], that dimer 7 is a II–II adduct.

Dimer 7 was transformed into a compound with the same molecular weight (MS) and a slightly higher retention time than the parent dimer (Fig. 4). The new compound (peak 10) is an isomer of 7 (iso-dimer 7) different from those present in the commercial mixture. The isomerization progressed until a dimer to iso-dimer ratio of 15:85; the same ratio was found by Weissberger and Page[10] for the isomerization of 2-methylnorbornene to 2-methyleneorbornane. This analogy suggests that the isomerization of dimer 7 results in the formation of an exocyclic double bond at the expense of that in the norbornene ring. The IR spectrum of the dimer to iso-dimer
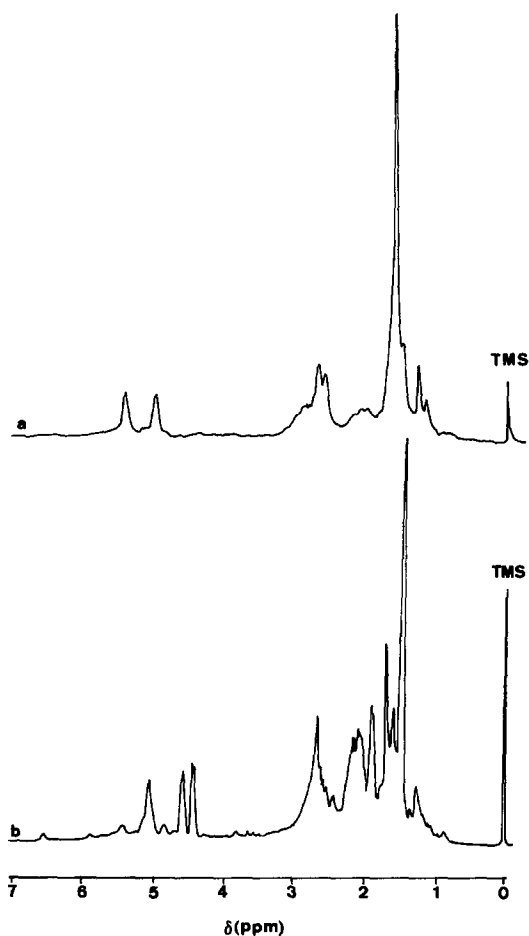
Fig. 3. ^{1}H NMR spectra of dimer 7 (a) and a mixture of dimer 7 and iso-dimer 7 (b).

mixture in Fig. 4b shows a new band at 880 cm^{-1} typical of terminal double bonds. Its ^{1}H NMR spectrum (Fig. 3b) shows that the signal at 5.45 ppm due to the olefinic hydrogen in the 2-methylnorbornene rings is almost extinguished and two new signals at 4.45 and 4.60 ppm have appeared. These new signals may be due to the two olefinic hydrogens of the exocyclic double bond since vinylic hydrogens in the exocyclic methylene group of 2-methylenenorbornane give signals at 4.47 and 4.72 ppm and those of 2-methylene-5-norbornene at 4.67 and 4.95 ppm[10].

Attempts to isolate the pure iso-dimer 7 by preparative GC were not successful since some reactions took place (probably oxidations) resulting in a mixture with 78% of the iso-dimer. Nevertheless, the ^{13}C NMR and off-resonance ^{13}C NMR spectra corroborate the existence of an exocyclic double bond by the signals at 104.38, 104.93, 151.76 and 151.86 ppm typical of terminal double bonds, and at 125.89 ppm due to $=$CH– groups. Cyclic compounds with an exocyclic double bond, such as 2-methylene-5-norbornene[10] and 4,4,7,7-tetramethyl-2-methylenebicyclo[3.3.0]-
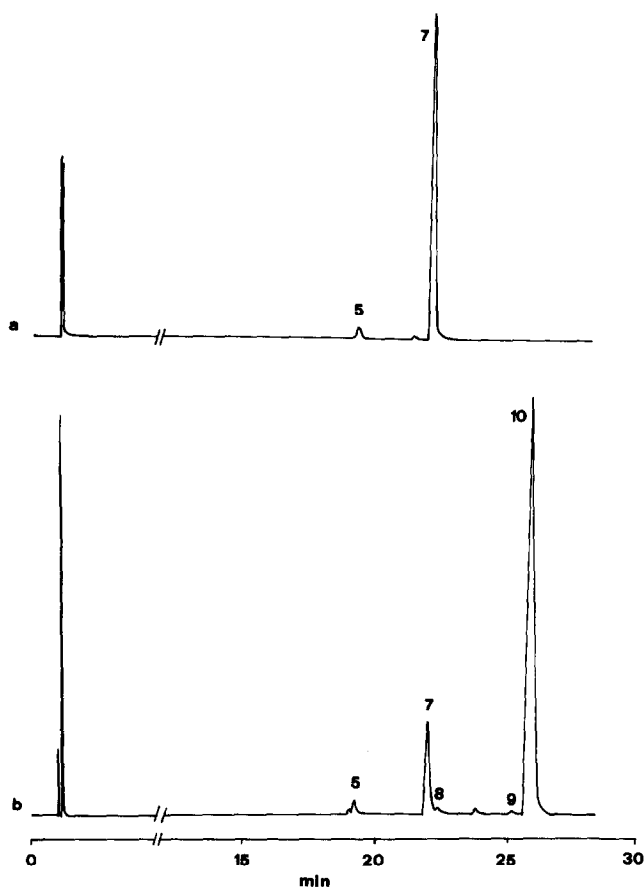
Fig. 4. Chromatograms of dimer 7 (a) and the mixture obtained upon its isomerization (b) on squalane at 100°C.

octane[11] show signals at similar positions. The off-resonance ^{13}C NMR spectrum shows two triplets at 104.38 and 104.93 ppm and two singlets at 151.76 and 151.86 ppm with the same coupling constant, which confirm the existence of carbon atoms in $>C=CH_2$ structures.

A mixture of dimers 4 and 5 (67:33) was isolated by preparative GC. The dimer 4 undergoes the same isomerization as that of dimer 7. The ^1H NMR spectrum of this mixture before isomerization shows identical signals to those of the commercial mixture, which reveals the coexistence of structures with both methylnorbornene rings. After isomerization of dimer 4, the spectrum shows the same signals, at 4.45 and 4.60 ppm, to those of the iso-dimer 7.

The common behaviour of dimers 4 and 7 and the identity of the signals of the olefinic hydrogens of their isomers suggest that 4 and 7 have the same methyl-norbornene ring in their structures, differing in the position of the methyl group in the cyclopentene ring. Therefore dimer 4 results from the addition of I (dienophile) to II
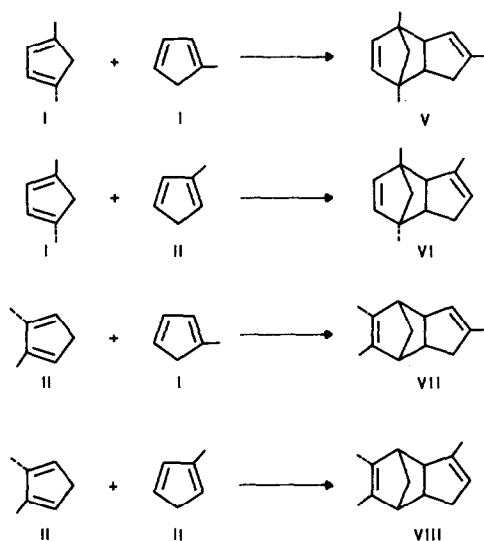
Fig. 5. Probable structures of dimers 2, 4, 5 and 7: I = 1-methyl-1,3-cyclopentadiene; II = 2-methyl-1,3-cyclopentadiene; V = 1,4- (or 4,7-) dimethyl; VI = 1,3- (or 3,7-) dimethyl-; VII = 4,8- (or 4,9-) dimethyl-; VIII = 3,8- (or 3,9-)dimethyl-*endo*-tricyclo[5.2.1.0^{2,6}]deca-3,8-diene.

(diene). Consequently, the 1-methylnorbornene ring in the mixture of dimers 4 and 5 belongs to dimer 5 one which should result from the addition of II (dienophile) to I (diene). Finally, judging by its low retention time and concentration, dimer 2 may be the result of a I–I dimerization. The structures in Fig. 5 clearly show why only dimers 4 and 7 (structures VII and VIII, respectively) are able to be transformed into isomers with an exocyclic double bond.

Some insight into the precise position of the methyl group in the norbornene ring can be obtained from the shifts of the signals of olefinic and methyl hydrogens caused by the isomerization. The ^{1}H NMR spectrum of the mixture resulting from the isomerization of dimer 7 (Fig. 3b) shows that the signal of the olefinic hydrogens in the cyclopentene ring shifts from 5.05 to 5.24 ppm, and that due to methyl hydrogens from 1.68 to 1.51 ppm. Since the shifts reflect changes in the displacement of the double bond, the actual position of this in the iso-dimer 7 can be envisaged from molecular models of the two possible structures of dimers 7 and their isomeric forms. It seems that the structure of iso-dimer 7 with the methylene group at C-8 accounts better for the above-mentioned shifts. Nevertheless, other possibility cannot be excluded.

CONCLUSIONS

This study of the composition of a commercial mixture of methylcyclopentadiene dimers carried out by capillary GC on several stationary phases and operating conditions reveals that the mixture consisted of seven components of dimeric nature.

The main dimers were those resulting from Diels-Alder reactions in which the

more reactive of the methylcyclopentadienes, the 2-methyl isomer, reacted as a diene giving rise to structures which include 2-methylnorbornene rings. These structures were the only over able to undergo isomerization, similar to that of 2-methylnorbornene to 2-methylenenorbornane, leading to iso-dimers with an exocyclic double bond.

With regard to the precise position of the methyl group in the 2-methylnorbornene ring, some insight might be gained from the observation of molecular models in relation to the shifts of the ^{1}H NMR signals of the olefinic and methyl hydrogens caused by the isomerization. It seems that isomerization of 8-methyl structures to 8-methylene ones would account better for the above-mentioned shifts. Nevertheless, other options cannot be excluded.

REFERENCES

1 K. Alder and H. J. Ache, *Chem. Ber.*, 95 (1962) 503.
2 S. M. Csicsery, *J. Org. Chem.*, 25 (1960) 518.
3 S. H. Langer, H. R. Melton, T. D. Griffith and J. Coca, *J. Chromatogr.*, 122 (1976) 487.
4 M. R. Musaev, S. M. Sharifova and M. A. Aliev, *Azerb. Khim. Zh.*, (1975) 43.
5 W. E. Franklin, *J. Org. Chem.*, 35 (1970) 1794.
6 V. P. Zharov, S. G. Montanari and L. M. Tumanova, *Zh. Anal. Khim.*, 39 (1984) 551.
7 W. O. McReynolds, *J. Chromatogr. Sci.*, 8 (1970) 685.
8 H. C. Brown and K. T. Liu, *J. Am. Chem. Soc.*, 97 (1975) 600.
9 S. Bank, C. A. Rowe, Jr., A. Schriesheim and L. A. Naslund, *J. Am. Chem. Soc.*, 89 (1967) 6897.
10 E. Weissberger and G. Page, *J. Am. Chem. Soc.*, 99 (1977) 147.
11 J. Ipaktaschi and G. Lauterbach, *Angew. Chem., Int. Ed. Engl.*, 25 (1986) 354.
12 L. A. Paquette, R. A. Galemno, Jr., J. C. Caille and R. S. Valpey, *J. Org. Chem.*, 51 (1986) 686.