

GAS CHROMATOGRAPHIC DATA AND IDENTIFICATION OF ISOMERIC PRODUCTS OF CYCLOADDITION REACTIONS OF CONJUGATED C5 DIENES

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Abstract

Dimers and codimers resulting from thermal cycloaddition reactions of 1,3-cyclopentadiene, isoprene, *cis*-1,3-pentadiene and *trans*-1,3-pentadiene were characterised in terms of their Kovats retention indices on a HP-PONA capillary column at 100°C. The proportion of individual isomers in dimerisation and codimerisation products under defined reaction conditions and their chromatographic characteristics were compared with published data. The chemical structure of isomer products was assigned on the basis of agreement between experimental and literature data.

Key words: cyclopentadiene; isoprene; 1,3-pentadiene; pyrolysis gasoline; retention indices; gas chromatography; codimers; structure identification.

1. Introduction

The present paper deals with the chromatographic characteristics and identification of isomeric products of thermal cycloaddition reactions of C5 dienes contained in pyrolysis gasoline which is one of the liquid products from steam cracking of various hydrocarbon feedstocks. It consists of C5-C12 hydrocarbons and contains substantial amounts of dienes and olefins. C10 hydrocarbons in pyrolysis gasoline are mainly products of thermal cycloaddition reactions of 1,3-cyclopentadiene (CPD), isoprene (ISP) and *cis*- and *trans*-1,3-pentadienes (cP, tP). Intentionally, not the term "Diels-Alder reactions" but "cycloaddition reactions" is used because, in addition to the [4+2]-cycloaddition reaction products, i.e., the so called Diels-Alder reaction, also the [4+4]- or [2+2]-cycloaddition reaction products of dienes can be present in pyrolysis gasoline. For the sake of brevity, the term dimer is used for the product of the cycloaddition reaction of two identical molecules of a diene while the term codimer is applied for that of two unequal molecules. The corresponding reactions are simplifiably called "dimerisation" and "codimerisation".

In order to find out which components in the multicomponent mixture of pyrolysis gasoline correspond just to the isomers of dimers and codimers of C5 dienes, reaction mixtures of thermal cycloaddition reactions of cyclopentadiene, isoprene and *cis*- and *trans*-1,3-pentadienes were analysed by gas chromatography. The results of the analyses were compared to the literature data. The chemical structure of the dimers and codimers mentioned above was not determined directly (by the structural analysis) but obtained from the data of the authors who had dealt with the structural analysis of the products of cycloaddition reactions of dienes and presented in their papers also chromatographic characteristics of the identified structures. In the present work, the following circumstances were considered to be unequivocal determination of the structure:

- for a given dimer/codimer, chromatographic characteristics obtained by measurement and those published by at least two different authors (or teams) matched (retention time or the order of the components' elution being the criteria) and, simultaneously, the relative content of the isomers found in the dimerisation/codimerisation product was in agreement with at least one reference, or
- measured and published Kovats's indices of the given dimer/codimer matched and, simultaneously, the found and published relative content of isomers in the dimerization/codimerisation product agreed.

The fundamental review by Duschek *et al.* [1], devoted to the identification of the products of homodimerisation reactions of conjugated C5 dienes, presents, besides own experimental results, also a summary of published knowledge on the structure of dimers. The authors determined the structure of individual substances by combining spectroscopic methods (¹³C NMR, IR), microdehydrogenation and ozonolysis. The position of the double bonds in the dimer molecules was determined by reacting a dimer or a mixture of dimer isomers with ozone which splits the molecule's double bond, and subsequent reducing the fragments to diols. The structures of the resulting diols were then compared to known standards. Microdehydrogenation helped to identify the six-membered ring dimers and to specify the mutual position of their alkylgroups. This was based on the fact that, by dehydrogenation, the six-membered ring cyclodimers yield benzene derivatives which can be easily identified by comparing to known standards, whereas four- or eight-membered ring dimers are cleaved to numerous products.

Structure analysis of the products of the Diels-Alder reaction of cyclopentadiene with *cis*- and *trans*-1,3-pentadiene is presented in a study by Ishii *et al.* [2]. Using the gas chromatography and ¹³C NMR spectroscopy, the authors identified the products formed by reacting 1,3-cyclopentadiene with a mixture of 1,3-pentadiene isomers, by a reaction between *cis*- and *trans*-1,3-pentadiene and by dimerization of *trans*-1,3-pentadiene alone. The structure of the products of the cycloaddition reactions in the system cyclopentadiene/isoprene was studied by Iwase *et al.* [3], Tomi *et al.* [4] and Zenkevich [5]. Two codimer substances, one with a norbornene structure and the other with a tetrahydroindene structure, were obtained by the preparative gas chromatography [3]. It was proved by ¹³C NMR spectrometry and GC analysis that the former substance consists of *exo*- and *endo*-isomers of 5-isopropenyl-2-norbornene in a ratio of 14:84 (145°C) or 41:59 (160°C) and does not correspond to 5-methyl-5-vinyl-2-norbornene. Theoretically, the latter (tetrahydroindene) substance could contain 5-methyl- or 6-methyl-tetrahydro-1*H*-indene but the authors demonstrated unequivocally that only one structure is present, namely, *cis*-5-methyltetrahydro-1*H*-indene. Identification of the products of cycloaddition reactions in the system cyclopentadiene-isoprene is included in a paper by Zenkevich, entitled "Application of molecular dynamics to chromatographic-spectral identification of isomeric products of organic reactions" [5]. In the paper [5], retention indices of codimers of cyclopentadiene with isoprene and dimers of isoprene are given. Indices relates to a chromatographic analysis performed with a temperature programme from 30-60°C to 180-250°C (He, 0.6 atm, split 1:30). As a chromatographic phase OV-101 (100% liquid methylsiloxane) was applied having the polarity index of 229 and being comparable with, e.g., the commercial capillary HP-PONA used by us. Zenkevich gives retention indices for 6 isomeric structures of isoprene dimers: 949, 952, 1018, 1021, 1061 and 1063. Most probably, dimers with the lowest retention times correspond to 1,4-dimethyl-4-vinylcyclohexane and 1,5-dimethyl-5-vinylcyclohexane. Diprene and limonene are eluted as the third and fourth components.

Thanks to studies mentioned above, it is presently possible to reliably assign chemical structures to the products formed by cycloaddition reactions of the conjugated C5 dienes even without the NMR analyses, just comparing chromatographic characteristics of the unknown components to those of the identified structures presented in the papers above. Chromatographic characteristics of the *endo*- and *exo*-dimers of 1,3-cyclopentadiene were taken from our preceding study [6] published in this Journal.

2. Experimental

GC analyses were performed on a Shimadzu GC-17 A version 3 instrument equipped with a HP-PONA capillary column. The analysis conditions are summarised in Table 1. The HP-PONA column contains a non-polar stationary phase based on dimethylpolysiloxane and is typically used for analysis of petrochemical hydrocarbon mixtures. To determine the Kovats retention index **RI**, selected samples were analysed isothermally at a column temperature of 100°C and mixtures of reference alkanes were added to the samples. It was found by repeating analyses the accuracy of Kovats indices was higher than 0.1 – 0.5 index units.

A GC coupled to a quadrupole mass spectrometer (Shimadzu GCMS-QP 2010) was used to determine the molecular weight of the components analysed. The data were processed using GC-MS Solution Version 2.0 (Shimadzu).

Dimers and codimers were prepared by Diels-Alder reaction of the corresponding monomers in a pressure stainless steel vessel. Reactions were conducted in the liquid phase under isothermal conditions at several temperatures using cyclohexane as solvent. Cyclopentadiene

(CPD) was prepared by thermal decomposition of 99.5% *endo*-dicyclopentadiene (*endo*-DCPD) in a reboiler under a distillation column with 18 theoretic plates. The distillate of pure CPD was cooled at the column head using a mixture of acetone and dry ice and was then kept at -20°C. Cyclohexane, isoprene, 1,3-pentadienes, *n*-nonane, *n*-decane, *n*-undecane, *n*-dodecane, *n*-tridecane, R-(+)-limonene and dipentene were of commercial origin (Sigma–Aldrich–Fluka).

Table 1. GC analysis conditions

Integration	Chromatography Station CSW32 software
Detector	FID
Column	Capillary HP-PONA
Column length	50 m
Inside column diameter	0.2 mm
Film thickness	0.5 µm
Column temperature program	a) 40°C for 5 min, increased at 7°C min ⁻¹ to 250°C, held for 5 min b) isothermal analysis at 100°C
Detector temperature	200°C
Injector temperature	250°C
Carrier gas, inlet pressure	Helium, 370 kPa (initial linear velocity 40 cm s ⁻¹)
Split ratio	120
Injection volume	0.1 µl

3. Results and discussion

3.1 Dimerisation of isoprene

Dimerisation of isoprene was studied at temperatures of 100, 160, 180 and 220°C. Reaction mixtures were analysed with chromatographic capillaries HP-PONA, DB-5 and Stabilwax-DB. It followed from the analyses of the reaction mixtures that, in the temperature range of 100/220°C, the thermal dimerization of isoprene yields seven components in non-negligible concentrations. The GC-MS analysis confirmed that all of these components have $M_w = 136$ and $C_{10}H_{16}$ molecular formula. In the text below, the components will be denoted as DISP 0 to DISP 6; the detail of the chromatographic analysis of the dimerisate in Fig. 1 shows their retention times in the HP-PONA column using a standard temperature programme (Table 1).

For the identification of the structures of isoprene dimers, the retention indices (*RI*), published in papers by Doering *et al.* [7] and Zenkevich [5], were used, together with weight ratios of the products in the dimerisate prepared under defined conditions [1]. When comparing the measured and published *RI* values of the dimers, the well-known fact was taken into account that, for the case of non-polar chromatographic phases (Squalan [7], OV-101 [5] and HP-PONA used in this study), these values are almost temperature-independent. In particular, mutual differences between the *RI* values of individual components, measured under chromatographic conditions similar to the published ones, were considered to be decisive. This is summarized in Tab. 2. Limonene was determined by comparing the retention times (*RT*) of the substance and the analytical standard. Unequivocal assignments were achieved for limonene (DISP 4), diprene (DISP 3) and 1-methyl-1-vinyl-2-isopropenyl-cyclobutane (DISP 0). For the third of these substances, the relative configuration of the substituents is unknown. Indisputably, the structures of the components DISP 1-2 correspond to dimethylsubstituted vinylcyclohexenes while DISP 5-6 to dimethylsubstituted cycloocta-1,5-dienes. If solely the data in the paper by Duschek *et al.* [1] is taken into account and assuming the correctness of the authors' identification, then the component DISP 1 found by us is 1,5-dimethyl-5-vinylcyclohexene, DISP 2 is 1,4-dimethyl-4-vinylcyclohexene, DISP 5 is 1,5-dimethyl-cycloocta-1,5-diene and DISP 6 is 1,6-dimethyl-cycloocta-1,5-diene. It can thus be summed up that, upon heating, isoprene undergoes not only the cycloaddition reactions.

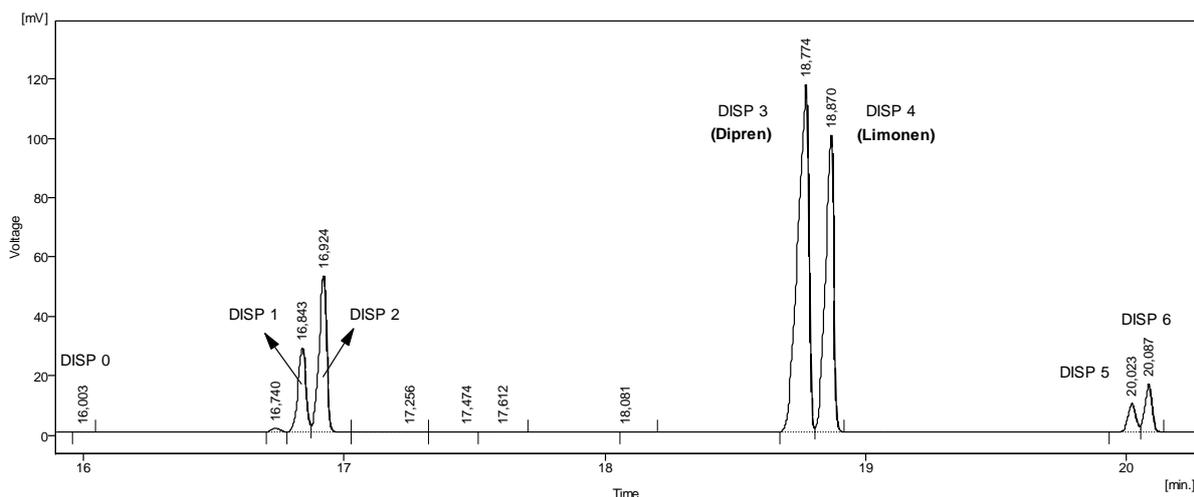


Figure 1. A cut-out from a chromatographic analysis of the isoprene dimerisate (*The HP-PONA column, standard analytical conditions*)

3.2. Cycloaddition reactions in the system cyclopentadiene – isoprene

Cycloaddition reactions of CPD with isoprene were studied at 70, 100, 120 and 140°C. At these temperatures, the reaction mixtures contained, in addition to the dimers of cyclopentadiene and isoprene, 6 components with MW=134, identified as codimers of cyclopentadiene with isoprene (CPD-ISP), as illustrated in Fig. 2. The dominant of them were the codimers CPD-ISP 2 and CPD-ISP 3, denoted in the literature as codimer A and codimer B [4, 8]. In a non-polar phase, the codimer A is eluted before *endo*-DCPD while the codimer B after it. In the reaction mixtures which at the beginning of the measurement contained less than 10% isoprene and CPD, and were exposed temperatures up to 120°C, the codimer A was present in amounts 5 to 8 times larger than the codimer B.

Chemical structures of the components CPD-ISP 1 to CPD-ISP 6 are presented in Table 3. Comparison of the experimental data with the published chromatographic characteristics [4, 5, 7] and other information on the formation of codimers CPD-ISP [3, 8, 9] enabled us to assign unambiguously chemical structures to all the six components CPD-ISP found in the reaction mixtures (see Table 3 and 8).

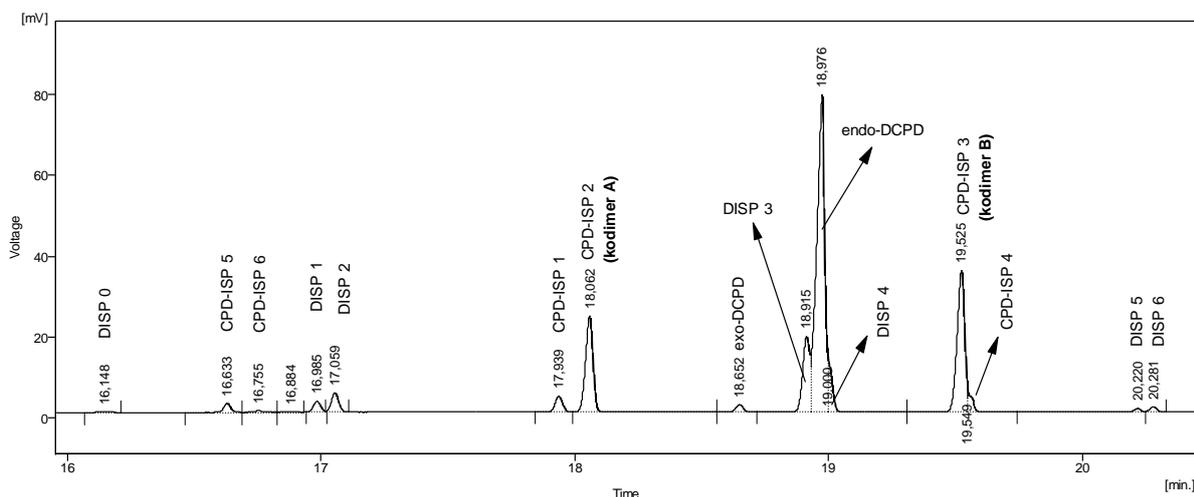


Figure 2. Products of cycloaddition reactions in the system cyclopentadiene – isoprene (140 °C, 14 hrs). A cut-out from the chromatographic analysis (*HP-PONA, standard analytical conditions*)

3.3. Dimerisation of *trans*-1,3-pentadiene

The dimerization of *trans*-1,3-pentadiene was followed at 100, 120, 140 and 180°C. In the given temperature range and using GC and GC-MS analysis, formation of 7 dimers was observed. They will be denoted below as DtP 1 to DtP 7. Their elution characteristics are given in Table 4. The separation in the HP-PONA chromatographic capillary is illustrated in Fig. 3. Elution characteristics measured and mutual ratios of the components in the dimerisate were compared to the literary data [1, 2, 7], as summarised in Table 4. It followed

from the comparison that the components DtP 1 and 2 are some of geometric isomers of 3,5-dimethyl-4-vinylcyclohexene and/or 3,4-dimethyl-5-vinylcyclohexene. The components DtP 3 and DtP 6 were identified unequivocally as *trans*- and *cis*-3-methyl-4-[(1*E*)-prop-1-en-1-yl]cyclohexene. According to the data given in the study by Duschek *et al.* [1], the components DtP 4 and 5, being eluted in a non-polar chromatographic column in between *cis/trans* isomers of 3-methyl-4-[(1*E*)-prop-1-en-1-yl]cyclohexene, correspond to *cis/trans* isomers of 3-methyl-5-[(1*E*)-prop-1-en-1-yl]cyclohexene but it is impossible to specify which component refers to *cis*- and which to *trans*-isomer. Most probably, the DtP 7 component is an isomer of 3,4- or 3,7-dimethylcycloocta-1,5-diene, the elution time of which corresponds to such a structure.

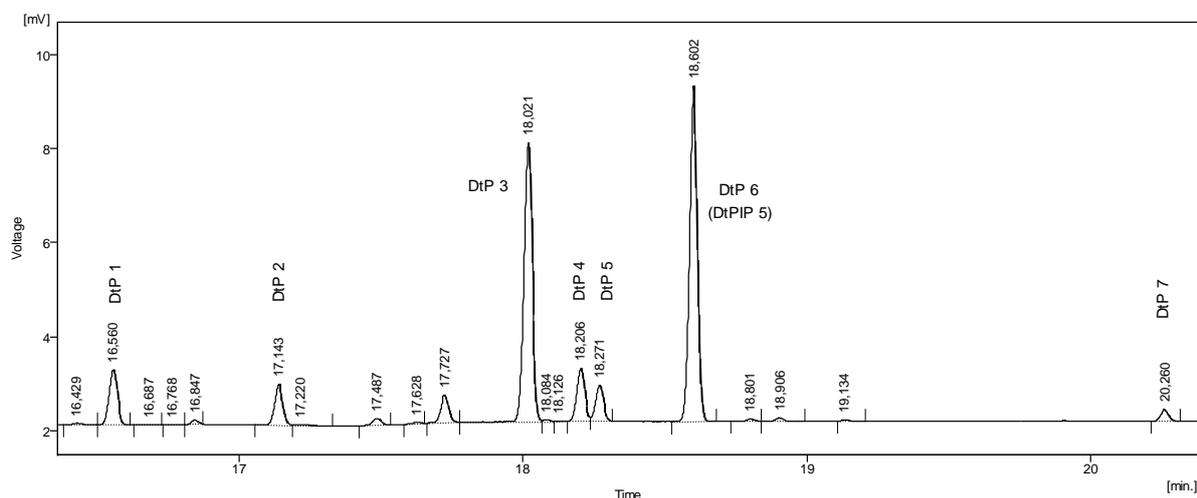


Figure 3. A cut-out from the chromatographic analysis of the dimerisate of *trans*-1,3-pentadiene (the HP-PONA column, standard analytical conditions)

3.4. Cycloaddition reactions in the system cyclopentadiene – *trans*-1,3-pentadiene

The reaction was followed at 60, 100, 120 and 140°C. Similarly to other cases, diluted solutions of the reactants in cyclohexane were used as the starting mixtures. Five components corresponding to the CPD-*trans*-1,3-pentadiene codimers (further denoted as CPD-tP) were found in the reaction mixtures. Elution characteristics and a comparison of experimental and literature data are given in Table 5. The separation in the HP-PONA GC column is elucidated in Fig. 4. Applying the data by Doering *et al.* [7] and Ishii *et al.* [2], chemical structures could unequivocally be assigned to the CPD-tP 3 to 5 codimers, namely, *endo*- and *exo*-5-[(1*E*)-prop-1-en-1-yl]-2-norbornene and 4-methyl-3a,7,7a-tetrahydro-1H-indene. The CPD-tP 1 and 2 components are *endo/exo*- isomers of 5-methyl-6-vinyl-2-norbornene which, however, could not be distinguished.

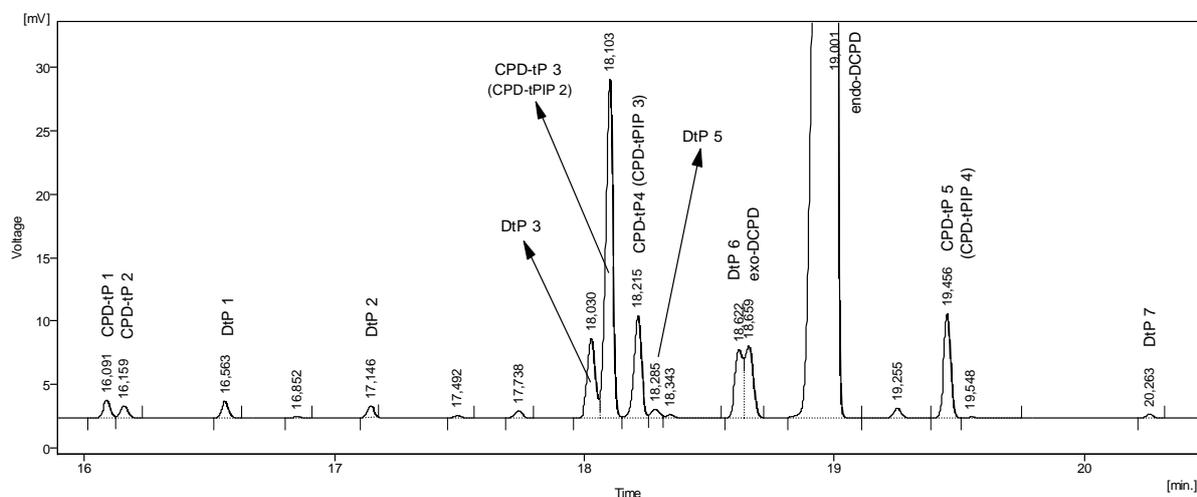


Figure 4. Products of cycloaddition reactions in the system cyclopentadiene – *trans*-1,3-pentadiene. A cut-out from the chromatographic analysis (HP-PONA, standard analytical conditions)

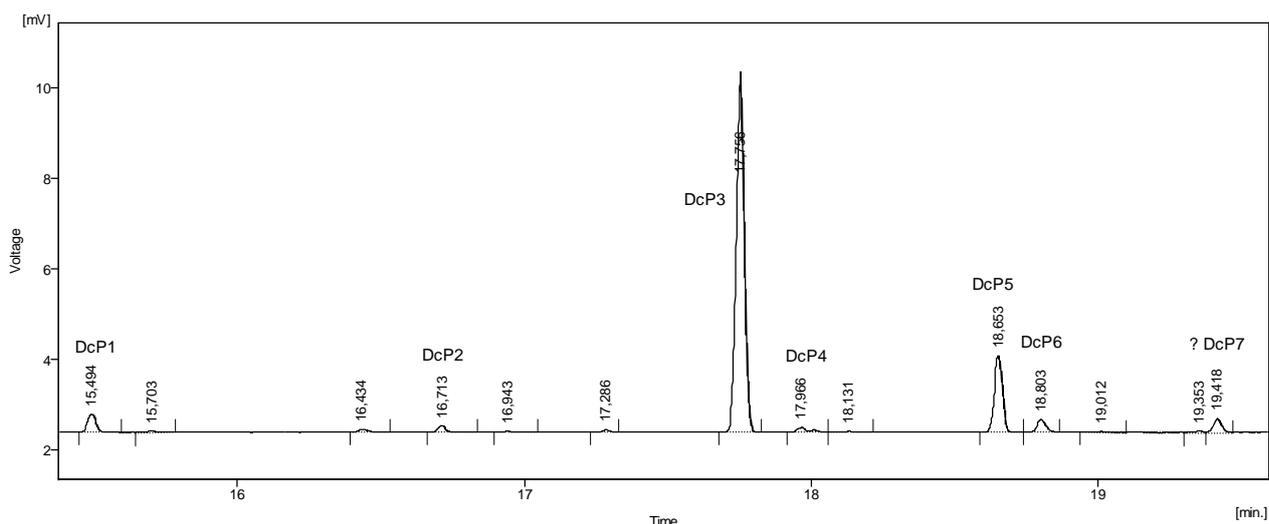


Figure 5. A cut-out from the chromatographic analysis of the dimerisate of *cis*-1,3-pentadiene.

3.5. Dimerisation of *cis*-1,3-pentadiene

Seven substances with the molar mass of 136 g/mol which corresponds to that of *cis*-1,3-pentadiene dimers were found in the respective reaction mixtures (Fig. 5). Unlike the products of cycloaddition reactions of other dienes under study, there is not enough information in the literature which would enable one to identify unambiguously the components. The structures of the dimers were only estimated, using primarily the data by Duschek *et al.* [1]. To make the estimation, both the order of the elution of dimers in a non-polar chromatographic phase and the ratio of the dimers in the reaction mixture (as obtained at 120°C) were used. The comparison is given in Table 6. Also, the following experimental fact was utilized to make the estimation: in a group of structure isomers and in non-polar GC phases, the isomers with a cyclobutane skeleton elute first, followed by the isomers with a cyclohexene skeleton and finally the isomers with a cyclooctadiene structure.

3.6. Cycloaddition reactions in the system cyclopentadiene – *cis*-1,3-pentadiene

Cycloaddition reactions in the system cyclopentadiene – *cis*-1,3-pentadiene were followed at 80, 100, 120 and 140°C. Besides the dimers of *cis*-1,3-pentadiene and *exo*- and *endo*-DCPD, several other components were found in the reaction mixture, the concentration of which increased with reaction time. Although a formation of 4 isomeric products of codimerisation of cyclopentadiene with *cis*-1,3-pentadiene (further CPD-cP) was described in the literature [2], only components having elution times of 18.19 min and 18.36 min (standard programme, HP PONA) could with certainty be identified as the CPD-cP codimers (Fig. 6), namely, as *exo*- and *endo*- isomers of 5-[(1*Z*)-prop-1-en-1-yl]-2-norbornene (cf. Table 7).

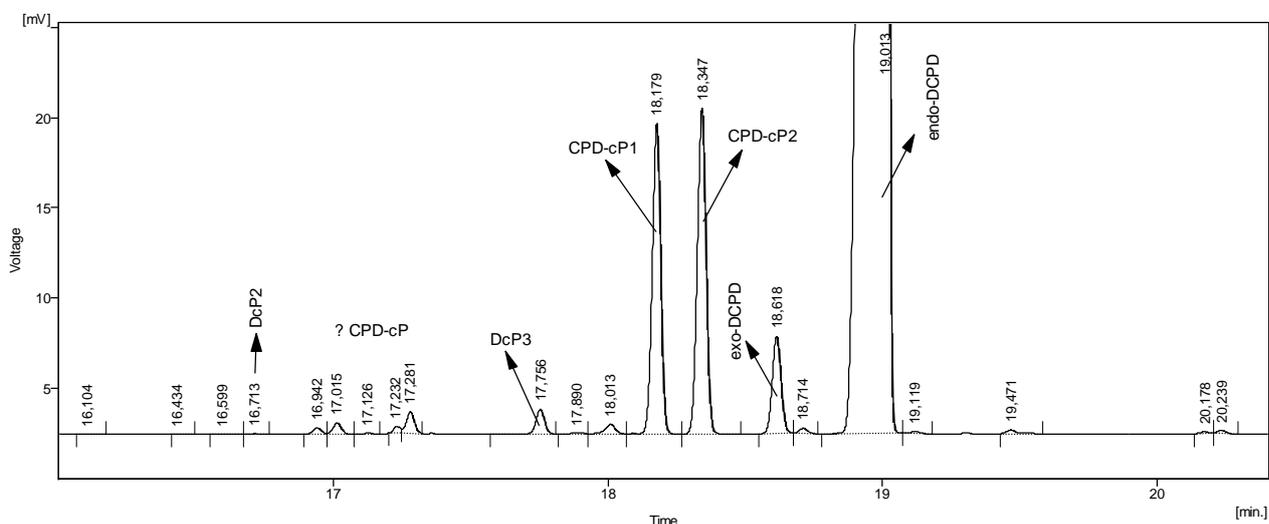


Figure 6. Products of cycloaddition reactions in the system CPD – *cis*-1,3-pentadiene. A cut-out from the chromatographic analysis (HP-PONA, standard analytical conditions)

4. Conclusions

Table 8 lists isomers of dimers and codimers of conjugated C5 dienes for which an unambiguous chemical structure was successfully assigned. These compounds were characterised in terms of their Kovats retention index on a HP-PONA capillary column at 100°C. Because isothermal GC analysis is not suitable for analysis of multi-component mixtures such as pyrolysis condensates, isomers were further characterised in terms of their retention time on a HP-PONA capillary column under a temperature programme (Tables 2 – 7).

Table 8. List of dimers and codimers with unambiguous assigned chemical structure

Label of a cycloaddition 1:1 adduct	Compound name	RI HP-PONA 100°C
DISP 3	1-methyl-5-isopropenyl-cyclohexene, (diprene)	1023.5
DISP 4	1-methyl-4-isopropenyl-cyclohexene (limonene)	1026.9
CPD-ISP 5	<i>endo</i> -5-methyl-5-vinyl-2-norbornene	950.3
CPD-ISP 6	<i>exo</i> -5-methyl-5-vinyl-2-norbornene	953.9
CPD-ISP 1	<i>exo</i> -5-isopropenyl-2-norbornene	991.4
CPD-ISP 2	<i>endo</i> -5-isopropenyl-2-norbornene (codimer A)	995.3
CPD-ISP 3	5-methyl-3a,4,7,7a-tetrahydro-1 <i>H</i> -indene (codimer B)	1044.2
CPD-ISP 4	6-methyl-3a,4,7,7a-tetrahydro-1 <i>H</i> -indene (codimer B)	1045.6
DtP3	<i>trans</i> -3-methyl-4-[(1 <i>E</i>)-prop-1-en-1-yl] cyclohexene	994.8
DtP6	<i>cis</i> -3-methyl-4-[(1 <i>E</i>)-prop-1-en-1-yl] cyclohexene	1014.6
CPD-tP 3	<i>endo</i> -5-[(1 <i>E</i>)-prop-1-en-1-yl] -2-norbornene	996.6
CPD-tP 4	<i>exo</i> -5-[(1 <i>E</i>)-prop-1-en-1-yl] -2-norbornene	1000.6
CPD-tP 5	4-methyl-3a,4,7,7a-tetrahydro-1 <i>H</i> -indene	1043.0
DcP 3	<i>trans</i> -1,2-di[(1 <i>Z</i>)-prop-1-en-yl] cyclobutane	985.5
CPD-cP 1	<i>exo</i> -5-[(1 <i>Z</i>)-prop-1-en-1-yl] -2-norbornene	1000.3
CPD-cP 2	<i>endo</i> -5-[(1 <i>Z</i>)-prop-1-en-1-yl] -2-norbornene	1005.9

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Symbols

CPD	1,3-cyclopentadiene
cP	<i>cis</i> -1,3-pentadiene
CPD-cP	codimer of cyclopentadiene with <i>cis</i> -1,3-pentadiene
CPD-ISP	codimer of cyclopentadiene with isoprene
CPD-tP	codimer of cyclopentadiene with <i>trans</i> -1,3-pentadiene
DcP	dimer of <i>cis</i> -1,3-pentadiene
DCPD	dicyclopentadiene, 3a,4,7,7a-tetrahydro-1 <i>H</i> -4,7-methanoindene
DISP	dimer of isoprene
DtP	dimer of <i>trans</i> -1,3-pentadiene
ISP	isopren
tP	<i>trans</i> -1,3-pentadiene
RI	Kovats retention index
RT	retention time [min] under the analysis conditions shown in Table 1

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Table 2. Isoprene dimers. Comparison of experimental and literature data.

Peak label	Experimental data		Published data		Duschek [1] isomer ratio* (115°C)	Doering [7] RI Squalane / PPG, 60°C	Zenkevich [5] RI OV-101 40-250°C
	RT [min] HP-PONA temp. prog.	RI HP-PONA 100°C	isomer ratio* (120°C)	Compound name			
DISP 0	16.15	932.5	1.1	1-Me-1-vinyl-2-isopropenyl-cyclobutane	2	909.6 / 980.5	
DISP 1	16.99	960.0	6	1,5-DiMe-5-vinylcyclohexene	6	943.9/1012.6	952
DISP 2	17.06	962.3	11.9	1,4-DiMe-4-vinylcyclohexene	14	943.4/1011.2	949
DISP 3	18.91	1023.5	46	Diprene	46	1008.2/1088.8	1018
DISP 4	19.00	1026.9	27.5	Limonene	28	1011.4/1092.3	1021
DISP 5	20.22	1068.3	1.7	1,5-DiMe-cycloocta-1,5-diene	1.3		? 1061
DISP 6	20.28	1070.5	3.2	1,6-DiMe-cycloocta-1,5-diene	2.7		? 1063

Bold indicates unambiguous assigned chemical structures.

Table 3. Identification of cyclopentadiene-isoprene codimer structures

Peak label	Experimental data		Iwase [3] isomer ratio** (145°C)	Muja [8] isomer ratio*** (140°C)	Doering [7] RI	Zenkevich [5] RI
	RT [min] HP-PONA temp. prog.	RI HP-PONA 100°C				
CPD-ISP 5	16.60	950.3	1.6		921.9 / 1006.7	923
CPD-ISP 6	16.72	953.9	1.0		925.3 / 1014.1	938
CPD-ISP 1	17.91	991.4	2.8	14	964.7 / 1058.0	970
CPD-ISP 2	18.03	995.3	35.4	84	966.2 / 1067.2	986
CPD-ISP 3	19.49	1044.2	7.5	7.7	1017.2 / 1114	1113
CPD-ISP 4	19.52	1045.6	0.7		1019.3 / 1117	1113
Reference material	18.63	1016	-		984.3 / 1019.4	
	19.06	1026	-		987.1 / 1099.8	1018

) in the dimerisation product, **) in the reaction mixture, *) in the reaction mixture after 1h.*

Table 4. *Trans*-1,3-pentadiene dimers. Comparison of experimental and literature data.

Peak label	Experimental data			Published data		Duschek [1]		Doering [7]		Ishii [2]
	RT [min] HP-PONA temp. prog.	RI HP-PONA 100°C	isomer ratio* (140°C)	Compound name	isomer ratio* (120°C)	order of elution CN-sil.**	RI Squalane / PPG 60°C	isomer ratio* (180°C)	order of elution Apiezon	
DtP 1	16.56	948.3	7.3	? (3,5)-DiMe-(4)-vinylcyclohexene	6	2	946.3 / 1000.4	5	1	
DtP 2	17.14	966.5	5.1	? (3,4)-DiMe-(5)-vinylcyclohexene	8	1		6	2	
DtP 3	18.02	994.8	35	trans-3-Me-4-[(1E)-prop-1-en-1-yl] cyclohexene	35	3	971.8 / 1034.8	51	3	
DtP 4	18.21	1000.6	6.2	<i>cis/trans</i> -3-Me-5-[(1E)-prop-1-en-1-yl] cyclohexene						
DtP 5	18.27	1002.7	4.3	<i>cis/trans</i> -3-Me-5-[(1E)-prop-1-en-1-yl] cyclohexene	10	4	985.3 / 1047.2			
DtP 6	18.60	1014.6	40.1	cis-3-Me-4-[(1E)-prop-1-en-1-yl] cyclohexene	41	5		38	4	
DtP 7	20.26	1070.8	2.7	(? 3,4)-dimethyl-cycloocta-1,5-diene	0	6	1050.0 / 1143.8			

*) in the dimerisation product, **) nitrile-silicone oil. Bold indicates unambiguous assigned chemical structures.

Table 5. Cyclopentadiene – *trans*-1,3-pentadiene codimers. Comparison of experimental and literature data.

Peak label	Experimental data			Published data		Doering [7]		Ishii [2]
	RT [min] HP-PONA temp. prog.	RI HP-PONA 100°C	isomer ratio** (140°C, 65h)*	Compound name	RI Squalane / PPG 60°C	isomer ratio** (180°C)	order of elution Apiezon	
CPD-tP 1	16.09	933.4	1.0	<i>endo</i> -5-Me-6- <i>exo</i> -vinyl-2-norbornene			908.1 / 990.4	1
CPD-tP 2	16.16	935.6	0.9	<i>exo</i> -5-Me-6- <i>endo</i> -vinyl-2-norbornene			906.5 / 989.1	1
CPD-tP 3	18.10	996.6	11.6	<i>endo</i>-5-[(1E)-prop-1-en-1-yl] -2-norbornene			968.2 / 1062.9	1 - 16 (?)
CPD-tP 4	18.20	1000.6	7.3	<i>exo</i>-5-[(1E)-prop-1-en-1-yl] -2-norbornene			973.8 / 1066.9	20
CPD-tP 5	19.46	1043.0	28	4-Me-3a,4,7a-tetrahydro-1H-indene			1015.9 / 1115.0	28

*) undiluted starting reactants in the molar ratio 1:1, **) in the reaction mixture. Bold indicates unambiguous assigned chemical structures.

Table 6a and 6b. Estimation of structures of *cis*-1,3-pentadiene dimers on the basis of a comparison with data given in literature

No. of compt.	Experimental data			Published data			Duschek [1]	
	Peak label	RT [min] HP-PONA temp. prog.	RI HP-PONA 100°C	isomer ratio* (120°C)	Compound name	RI Squalane / PPG 60°C		isomer ratio* (120°C)
1	DcP 1	15.49	911.3	3,2	? geometric isomer of 1-Me-2-vinyl-3-[(1Z)-prop1-en-1-yl]cyclobutane	?	4	1
2	? DcP 2	16.71	951.0	1,4	? geometric isomer of 1-Me-2-vinyl-3-[(1Z)-prop1-en-1-yl]cyclobutane	?	1	2
3	DcP 3	17.75	985.5	75	trans-1,2-di[(1Z)-prop-1-en-yl]cyclobutane	?	75	3
4	DcP 4	17.97 (? 2 compt.)	993.2	4.2	? <i>cis</i> -3-Me-5-[(1Z)-prop-1-en-1-yl]cyclohexene***)	983.4 / 1048.3		?
5	DcP 5	18.65	1016.3	13.8	<i>cis</i> -1,2-di[(1Z)-prop-1-en-yl]cyclobutane	?	5	4
6	DcP 6	18.80	1021.9	4.6	? <i>trans</i> -3-Me-5-[(1Z)-prop-1-en-1-yl]cyclohexene****)	990.2 / 1055	10	4
7	? DcP 7	19.42	1043.6	4.7	<i>cis/trans</i> -3,4-dimethyl-cycloocta-1,5-diene	?	4.7	5
					<i>cis/trans</i> -3,7-dimethyl-cycloocta-1,5-diene	?	0.3	5

*) in the dimerisation product **) nitrile-silicone oil, ***) *Ishii et al.* [2] state the opposite order of isomers

Table 7. Cyclopentadiene – *cis*-1,3-pentadiene codimers. Comparison of experimental and literature data.

Peak label	Experimental data			Published data			Ishii [2]
	RT [min] HP-PONA temp. prog.	RI HP-PONA 100°C	isomer ratio** (120°C, 1h)*	Compound name	RI Squalane / PPG 60°C	isomer ratio** (180°C)	
	?			<i>endo</i> -5-Me-6- <i>endo</i> -vinyl-2-norbornene <i>exo</i> -5-Me-6- <i>exo</i> -vinyl-2-norbornene	?		
CPD-cP 1	18.19	1000.3	48	<i>exo</i>-5-[(1Z)-prop-1-en-1-yl] -2-norbornene	969.1 / 1063.9	7	1
CPD-cP 2	18.36	1005.9	52	<i>endo</i>-5-[(1Z)-prop-1-en-1-yl] -2-norbornene	972.2 / 1070.5	72	2

*) undiluted starting reactants in the molar ratio 1:1, **) in the reaction mixture. Bold indicates unambiguous assigned chemical structures.