Formation and spectra of tri-methyl-cyclopentadienes

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PROEFSCHRIFT

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CHAPTER I

INTRODUCTION

The work going to be described in this thesis was not planned that way. The main objective was to show by examples a number of the features of the modern analytical tools of the organic chemist, and more in particular the integrated use of the methods of separation and isolation on the one hand, and the methods of identification on the other hand. Among the methods of separation and isolation distillation and chromatography, gas liquid chromatography in particular, have reached a high degree of perfection. These methods provide the samples for investigation by means of mass spectrometry, ultraviolet and infrared absorption spectroscopy and nuclear magnetic resonance techniques.

It was believed that terpenes, as a class of natural products, constitute a rich variety of prefabricated organic molecules. The structures of these molecules obey a number of rules and these rules have been a great asset in the elucidation of structures of terpenes by classical means. The following example may justify the choice of terpenes. It is a class of substances that has been studied extensively, but our knowledge still shows large gaps. Almost all terpenes can be conceived as derivatives of head to tail condensation products of isoprene. The simplest condensation, a straightforward dimerisation yields a 2.6-dimethyl-octane skeleton with three olefinic bonds.Excluding accumulated double bonds there are no less than 42 manners in which these double bonds can be distributed along the chain. Out of these 42 possible isomers there occur only three in nature, vis. myrcene and the two ocimenes. Thermal treatment of other natural terpenes appeared to yield the two allo-ocimenes. The remaining 37 isomers are still to be detected. Also the question why 3 or 5 isomers among 42 take the exceptional position remains largely unanswered.

The means and the base materials having been defined,there remains one item to be discussed. New substances, new discoveries are possible in the terpenes as such. The chance, however will be greater if the terpenes are subjected to (simple) chemical reactions. In order to avoid involved synthesis work the investigation has been confined to a number of simple and preferably clean reactions: ester thermolysis and thermal isomerisation of hydrocarbons. In one case the acid dehydration of alcohols was applied.

Among the reactions studied it appeared that the thermolysis of certain bicyclic terpene alcohol acetates did not proceed completely to expectations. When the thermolysis of the acetates is carried out under conditions more severe than to cause only the concerted or quasi-heterolytic elimination of acetic acid, subsequent reactions occur. Under the most severe conditions the observed products are most probably formed by free-radical processes. In the intermediate range other reactions took place, firstly a retro-Diels-Alder reaction, the mechanism of which is the subject of many investigations. Secondly the interconversions of the resulting tri-methyl-cyclopentadienes were observed. The question arose, whether the latter constituted a representative of what have been called in irony "no mechanism" reactions. (ref 1). More particularly it is of interest whether a sigmatropic reaction occurs.Such isomerisations are characterised by the shift of a sigma bond and are known to accur in ions and, thermally or photochemically, in molecules. If the trimethyl-cyclopentadienes isomerised by such a process, the reaction would show a novel feature. In known thermal sigmatropic reactions an allyl group (Cope reaction) or a hydrogen atom is shifted. The thermal isomerisation of the tri-methyl-cyclopentadienes would be a first example in which a methyl group is shifted.

A substantial part of this thesis deals with mechanistic studies concerning the isomerisation reactions and with the structure confirmation of reactants and products.If tri-methyl-cyclopentadienes are subjected to a Diels-Alder synthesis with ethylene as the dienophylic agent, the re-

action products are tri-methyl-norbornenes. These and other strained bicyclic compounds represent an interesting class of subjects which were studied by means of nuclear magnetic resonance spectroscopy.

CHAPTER II

THERMOLYSIS OF FENCHYL-, BORNYL- AND ISOBORNYL ACETATE

II-1 Introduction

Ester thermolysis has for a long time been useful in the synthesis of a large number of unsaturated compounds (refs 2,3,4). The overall reaction is given by:

$$\text{ester} \xrightarrow{\text{heat}} \text{olefin} + \text{acid}$$

Ester thermolysis in the gas phase was first introduced in 1876 by OPPENHEIM and PRECHT (ref 5).As a rule the reaction is comparetively clean, in contrast to the results obtained by dehydration of the corresponding alcohols in acid medium, where in most cases the reaction product consists of a mixture of isomeric olefins. An important example with respect to synthetic value was reported by WHITMORE and ROTHROCK who subjected 3.3-dimethyl-butyl-2-acetate to thermolysis and obtained 3.3-dimethyl-butene-1 uncontaminated by isomers (ref 6). Dehydration of the corresponding alcohol yields a mixture of three isomers. Thermolysis proceeds via cis-elimination of the β-hydrogen. Thus only one isomer is usually formed in the case of a primary acetate. Secondary and tertiary acetates with more β-hydrogens yield mixtures. The relative amounts of the isomers formed are governed largely by statistical and sterical effects (refs 7,8). Sometimes the relative thermodynamical stabilities of the products play an important role,especially in the case of endo- or exocyclic olefins. For further details and examples concerning the mechanism and the applications of ester thermolysis the reader is referred to the extensive reviews of SCHEER and DE PUY (refs 9,10).This study is concerned mainly with the thermal degradation reactions of the bicyclic esters isobornyl-, bornyl- and fenchyl acetate and with the subsequent secondary reactions of the primary thermolysis products.

This chapter deals, firstly, with the rates of thermolysis, as studied in a microflow reactor.Secondly the natures

and amounts of the reaction products were determined as functions of the temperature and the contact time. These experiments were performed in a macroflow reactor. Finally the results are summarised, discussed and compared with previously published data.

II-2 Experimental

II-2-1 Starting materials

a. Isobornyl acetate (Firmenich).
From GLC-analysis on two columns (4 m Apiezon-L at 140°C and 4 m PEG at 110°C) a total impurity of about 3% could be estimated. It was used without further purification.

b. Bornyl acetate (Firmenich)
GLC-analysis revealed a purity of about 88%. The main impurity appeared to be isobornyl acetate. A considerable purification was effected by thermolysing the raw material in the macroflow reactor at 400°C with a contact time of about 25 secs.Under these conditions the isobornyl acetate was converted to hydrocarbons almost quantitatively whereas most of the bornyl acetate remained unaffected. After distillation of the thermolysate to remove the hydrocarbons the purity was estimated at 97% by GLC.

c. Fenchyl acetate (K&K Labs)
The initial purity was found to be approximately 68%, the main impurities being bornyl- and isobornyl acetate. It was treated in a similar way as bornyl acetate but at a temperature of 540°C at which both contaminants were converted to hydrocarbons and acetic acid . After distilling off the hydrocarbons a purity of about 98% was obtained.

II-2-2 Macroflow reactor

This reactor was originally designed to enable thermolysis at rates of approximately 50 g/hr in order to obtain suitable quantities for the isolation of pure components. The isolation methods usually involved distallation and preparative gaschromatography. Thermolysis intakes of about 100 g appeared to be quite useful.
The outer alumina wall was covered with an asbestos jacket to reduce heat losses. The two inner concentric cylinders

were made of silver, a metal of high thermal conductivity, thus making the temperature homogeneity as good as may be expected for such a large reactor. Between the outer silver cylinder and the alumina wall a jacket of isolating material contained the heating wires. The temperature was controlled by regulating the electric energy supply with the aid of a pair of Variacs. Temperature measurements were carried out with two thermocouples (Chromel-Alumel).

The reactor tube, which consisted of a copper or pyrex glass spiral, was placed between the two concentric silver cylinders. Four different tubes were used:

No.	Material	I.D.	Length	Volume
1	Copper	1.0 cm	1000 cm	840 cm^3
2	Pyrex	0.7 cm	1000 cm	420 cm^3
3	Pyrex	0.7 cm	500 cm	210 cm^3
4	Pyrex	0.7 cm	250 cm	105 cm^3

With this set of tubes it was possible to vary the contact times over a rather wide range without necessitating very fast carrier gas velocities and thus avoiding turbulence effects. The contact times were controlled via the carrier gas velocities by means of the needle control valve of the nitrogen cylinder. The gas velocity was measured with the aid of a rotameter, which was checked against a wet gas volumeter. Corrections required for carrier gas heating were made. No corrections were applied for the expansion of the sample on evaporation in the reactor.

The reactant was introduced via a dropping funnel into the carrier gas stream. A 40 cm long copper tube, surrounded by a heating wire, served as an evaporator for the reactants and as a preheater for the carrier gas. Of course such a dropwise introduction of the reactant is not very suitable for obtaining very reproducible and constant residence times because some irregularities in the speed of the sample introduction and evaporation in the preheater can hardly be avoided. Therefore the macroreactor was not very suitable for obtaining kinetic data.

The reaction products were condensed in a trap, cooled with ice. The acetic acid was neutralised with a sodium bicarbonate solution after which the mixture was washed

several times with water and finally dried over anhydrous calciumchloride. The hydrocarbon mixture was analysed by GLC on an Apiezon-L column, operated at 80°C.

II-2-3 Microflow reactor

The reactor, described in the previous section has been used for the preparation of decomposition products. For the measurement of certain reaction constants the macro reactor has a number of obvious disadvantages because it has been designed for production. The same applies to most reactors described in literature. The accurate measurement of conversions and thus of reaction rates, rate constants and entropies and energies of activation of homogeneous gas reactions with this type of reactor has always been rather cumbersome. It is believed that the microflow reactor method to be described below has the advantages of being rapid and accurate.

The microflow reactor has been designed in this laboratory; it permits accurate control of temperatures and residence times. It has a considerable thermal capacity and the materials used guarantee a high thermal conductivity and a good temperature homogeneity. The reactor proper is a gold tube of 900 mm lenght and 1 mm I.D. It is coiled around a silver core and surrounded by a silver jacket. It will be described in full detail in a forthcoming thesis by Cramers.

It was shown (ref 11) that the results obtained by pulse operation are equivalent to those, obtained with continous flow, provided the reaction proceeds by first-order kinetics. Pulse operation has the advantage, that only very minute amounts of material are required. This is especially important in the case of the hydrocarbon isomerisation reactions, described in chapter III, since isolation of these compounds in substantial amounts is rather time-consuming.

The device for measuring reaction kinetics consisted of the microflow reactor, a high resolution gas chromatograph and an electronic integrator with voltage to frequency converter. There were two separate nitrogen carrier gas streams, one for the reactor and one for the chromatograph.

They were operated independently. The advantages of such a parallel system have been discussed by RUMMENS (ref 12). The GLC column used was of the capillary type. During the investigations of the acetate thermolysis a 30 m Apiezon-coated column was used at 140°C. Under these conditions the retention times of the acetates were about 20 mins. Unfortunately the components of the reaction mixture could not be integrated separately because the differences in retention times were too small.
The residence times were determined by measuring the nitrogen carrier gas stream by means of a soap bubble flow meter. In the calculations it was assumed, that no volume change occurred during the reactions. Of course any ΔV changes the flow rate and thus the contact time. In the macroflow reactor, where the reactants are added dropwise to the carrier gas stream this effect may be important. In the microflow reactor the amount injected is only 0.1 µl liquid, corresponding with approximately 50 µl gas. This was relatively small compared with the reactor volume of 700 µl. The reactor temperature was measured by means of a thermocouple to which a recorder was connected with continously adjustable span and zero point. During the course of one series of measurements the temperature was raised gradually by means of the electric energy supply. (see ref 11). During one measurement the temperature was averaged by interpolation between the temperatures at the moments of the injection in the reactor and emerging from the reactor (as calculated from the residence times).

The amounts of conversion of bornyl- and isobornyl acetate were determined in two ways: with fenchyl acetate as an internal reference or without. In the latter case the relative amounts of unreacted and converted acetate could be deduced from a comparison of the area of the acetate signal and the total integrated areas of all product signals respectively. The measurement of the reactor outlet gas composition was performed by means of a flame ionisation detector. The signal area, corresponding to a given number of molecules is in this case only dependent on the numbers of C- and H-atoms per molecule. It was shown that addition of fenchyl acetate did not alter the decomposition pat-

terns of the other acetates and that fenchyl acetate did not shown any conversion at the temperatures applied.

II-2-4 Discussion of the relative errors.

RUMMENS (ref 12) discussed the requirements of a micro-flow reactor. He estimated the errors, made in the calculations of reaction rates when the average residence time is used instead of taking into account its distribution. This distribution is caused by molecular diffusion, reactor type, streamline profiles, concentration-, temperature- and pressure gradients. For his reactor, which consisted of a tube of 10.000 mm lenght and of 1 mm I.D. the sum of the effects was shown to be of the order of 0.02%. For the reactor, used in this study in the same way an error of 0.2% maximum could be made so that the mean residence times might be used in the calculations without introducing a large error.

If $F = Co/c$, than $k = 1/t \ln F$ for a first order reaction and thus:

$$\frac{\Delta k}{k} = \sqrt{\left(\frac{\Delta t}{t}\right)^2 + \left(\frac{\Delta F}{F \ln F}\right)^2}$$

The error in t was about 2% maximum. $F = Co/C$ where $Co = Z.S$ in which S is the concentration of the internal standard from which Co was calculated by multiplication with the calibration factor Z. The errors in Z and S were 1% each.

so: $$\frac{\Delta C_o}{C} = \sqrt{\left(\frac{\Delta Z}{Z}\right)^2 + \left(\frac{\Delta S}{S}\right)^2} = 1.4\%$$

and: $$\frac{\Delta F}{F} = \sqrt{\left(\frac{\Delta C}{C}\right)^2 + \left(\frac{\Delta C_o}{C_o}\right)^2} = 1.7\%$$

since $\frac{\Delta C}{C} = 1\%$

$$\frac{\Delta k}{k} = \sqrt{\left(\frac{\Delta t}{t}\right)^2 + \left(\frac{\Delta F}{F \ln F}\right)^2}$$

The error in k depended upon the conversion. In this work the mean conversion was about 50%, so F = 2.

$$F = 2 \qquad \ln F = 0.69$$

From which:

$$\frac{\Delta k}{k} = \sqrt{\frac{4.0}{10^4} + \frac{2.9}{0.69 \times 10^4}} = 2.9\%$$

It remained to estimate the error in k as a consequence of errors in the temperature T.

From $k = k_o \, C^{\frac{-E}{RT}}$ it followed that:

$$\frac{dk}{dT} = \frac{kE}{RT^2} \qquad \text{or:} \qquad \frac{\Delta k}{k} = \frac{E}{RT^2} \Delta T$$

in which $E \simeq 40.000$ cal mole^{-1} $\quad R = 1.98$ cal mole^{-1} degr^{-1}

$T \simeq 700\ ^{o}k \quad \Delta T = 1\ ^{o}K$

From these values it followed that $\frac{\Delta k}{k} = 4.1\%$.

The total error in k was caused both by temperature variations and by errors in t and F. The total relative error is:

$$\frac{\Delta k}{k} = \sqrt{\left(\frac{4.1}{10^2}\right)^2 + \left(\frac{2.9}{10^2}\right)^2} = 5.0\%$$

at 50% conversion.

The maximum relative error in k is 5.0%, making the maximum relative error in ln k = 1.6% and in Δ ln k = 1.6 x 1.4 = 2.2%. The error in T depends largely on the way in which the temperature is controlled and measured. In this study the measurements were extended over a range of 60^{o}K. The relative error in T could be reduced to about 3% by increasing or decreasing the temperature at a rate of 0.2^{o}K/min (see ref 11). The reaction temperature was found by

 interpolation between the temperature at the moment of

injection in the microreactor and the moment at which the gas mixture emerged from the reactor. The maximum relative error in $\frac{\Delta 1/T}{1/T}$ was thus about 3 x 1.4 = 4.2%.

by which: $\frac{\Delta(E/R)}{E/R} = \sqrt{\frac{(2.2)^2 + (4.2)^2}{10^4}} = 4.7\%$.

II-3 Results

II-3-1 Reaction rates, energies and entropies of activation

In tables II-2 and II-3 experimental data on temperatures, residence times and conversions are given together with values of k and log k, derived from them. In fig II-1 the logarithm of the rate constant is plotted against the reciprocal temperature.

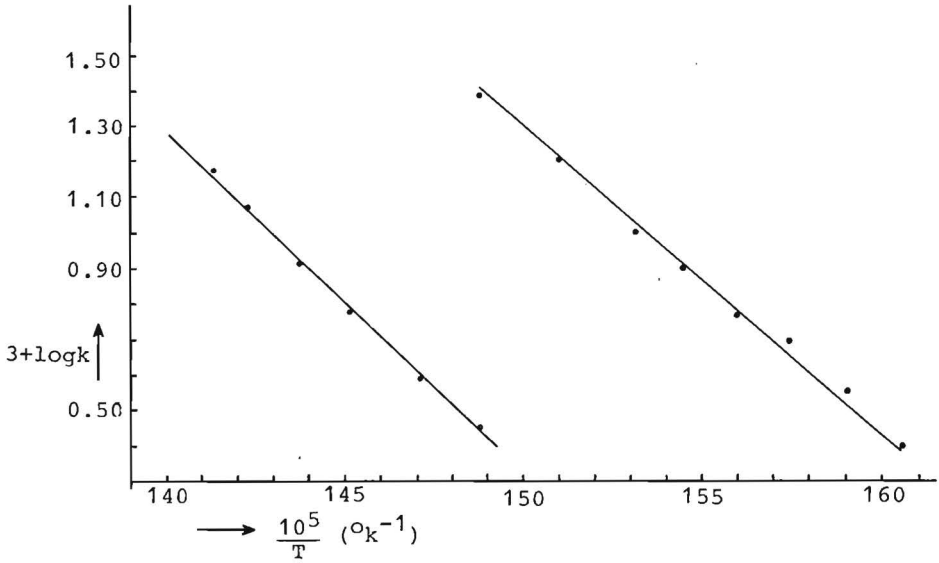


fig II-1 Thermolysis rates of a) Isobornyl acetate
b) Bornyl acetate

The resulting parameters for the Aerhenius equation and for the equation for absolute rate constant:

$$k = \frac{k\,T}{h} e^{S/R} e^{-H/RT}$$

Table II-2 Thermolysis of isobornyl acetate

Temp (°C)	$\frac{10^3}{T}$ ($^\circ K^{-1}$)	τ (sec)	$\frac{C_o}{C}$	$\log \frac{C_o}{C}$	$\frac{10^3}{\tau} \log \frac{C_o}{C}$ (sec^{-1})	10^3 k (sec^{-1})	3 + log k
345.8	1.616	71.7	1.199	0.0792	1.105	2.545	0.4057
355.8	1.590	70.6	1.283	0.1084	1.535	3.535	0.5481
362.3	1.574	69.9	1.431	0.1562	2.235	5.147	0.7115
367.8	1.560	69.3	1.511	0.1800	2.597	5.981	0.7768
374.2	1.545	68.7	1.792	0.2537	3.693	8.505	0.9297
380.3	1.531	67.9	2.000	0.3031	4.464	10.281	1.0020
388.7	1.511	67.1	2.877	0.4590	6.841	15.755	1.1973
394.3	1.498	66.5	4.099	0.6124	9.209	21.208	1.3265
398.6	1.489	66.1	5.076	0.7037	10.646	24.518	1.3895

Table II-3 Thermolysis of bornyl acetate

Temp (^{o}C)	$\frac{10^3}{T}$ ($^{o}K^{-1}$)	τ (sec)	$\frac{C_o}{C}$	$\log \frac{C_o}{C}$	$\frac{10^3}{\tau} \log \frac{C_o}{C}$ (sec^{-1})	10^3 k (sec^{-1})	3 + log k
399.1	1.488	66.0	1.233	0.0810	1.227	2.826	0.4512
407.0	1.471	65.3	1.297	0.1129	1.729	3.982	0.5901
416.0	1.451	64.4	1.479	0.1700	2.640	6.080	0.7839
422.2	1.438	63.8	1.692	0.2284	3.580	8.245	0.9162
429.5	1.423	63.2	2.119	0.3261	5.160	11.883	1.0748
434.8	1.413	62.7	2.544	0.4055	6.467	14.893	1.1729
440.4	1.402	62.2	5.000	0.6990	11.238	25.881	1.4130

in which: k = reaction constant
k = Bolztmann's constant
h = Planck's constant
e = base of natural logarithms
R = gas constant
are given in table II-1

Table II-1 Acetate thermolysis.

Compound	^{10}log A	E (kcal/mole)	H (kcal/mole)	S (cal/mole degr)
Isobornyl acetate	11.16	39.1	37.8	- 9.0
Bornyl acetate	10.42	39.7	38.3	-12.5

II-3-2 Thermolysis products of fenchyl acetate.

Fenchyl acetate was converted into cyclofenchene and acetic acid only. At a reaction temperature of 465°C and residence times varying from 2.4 to 40 secs the conversion was 0.8-10%. A complete conversion was only obtained at temperatures above 550°C. At temperatures above 600°C cyclofenchene is unstable.

II-3-3 Thermolysis products of isobornyl acetate

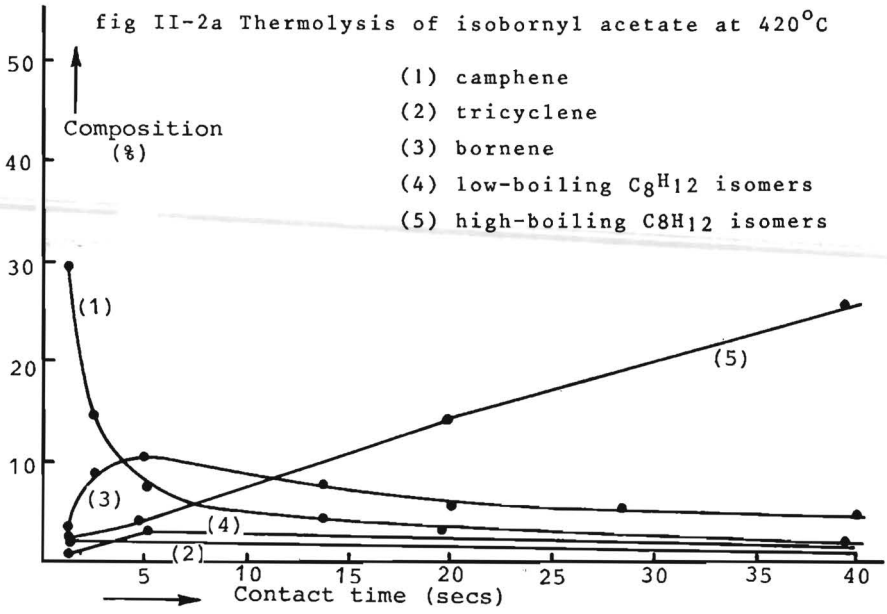
The minimum temperature,at which an appreciable conversion of isobornyl acetate was obtained in the macroreactor, was about 420°C. A conversion of 34% was reached with a residence time of 2.6 secs. The major product was camphene (29%) with 2% tricyclene and also some 2% bornene. These figures are to be considered as mean values since the results were not very reproducible. Wall effects may have been involved, although no better reproducibility was obtained when the copper spiral was replaced by a glass one.

 At higher temperatures and/or longer residence times de-

creasing amounts of terpenes were formed. Simultaneously increasing percentages were found of four compounds which turned out to be tri-methyl-cyclopentadienes (C_8H_{12}) but surprisingly the total conversion decreased somewhat; the amount of bornene went through a maximum. These trends suggest that one or more of the three observed terpenes act as intermediates in the formation of the C_8H_{12} isomers. Under these conditions, however, camphene and tricyclene, either alone or in the presence of an equimolar amount of acetic acid were found to be stable. Bornene however, either alone or in the presence of acetic acid yielded the four C_8H_{12} compounds and ethene. The results are shown in fig II-2.

Isobornyl acetate is virtually completely converted at 460°C and a residence time of about 5 secs. Under these conditions a number of "new" products is formed.
The four isomeric tri-methyl-cyclopentadienes (TMCPD's) could be distinguished into a pair of low boiling isomers (96°C and 99°C), and a pair of higher boiling compounds (126°C and 129°C). It was obvious from the experimental results, that the low boiling TMCPD's are the primary decomposition products of the $C_{10}H_{16}$ intermediate(s?). The high boiling isomers are formed subsequently by rearrangements of the low boiling pair. At temperatures up to 500°C the highest boiling isomer (129°C) predominates clearly in the reaction mixture. At temperatures between 500°C and 600°C, however, almost equal portions of both high boiling isomers are found. This suggests, that one of the two (126°C) is formed from the other (129°C) in a further rearrangement reaction. These C_8H_{12} isomerisation reactions are to be discussed in detail in chapter III. At 475°C the first traces (2-3%) are found of a "compound" which was identified as C_6H_8 by mass-spectrometry. It turned out to be a mixture of mono-methyl-cyclopentadienes as was shown by NMR- and IR spectroscopy. Toluene was detected in a similar way. The percentage of bornene diminished gradually with increasing temperatures and residence times. At 520°C a new group of approximately eight compounds was observed by GLC analysis.A complete separation by preparative gaschromatography was not achieved.

fig II-2a Thermolysis of isobornyl acetate at 420°C



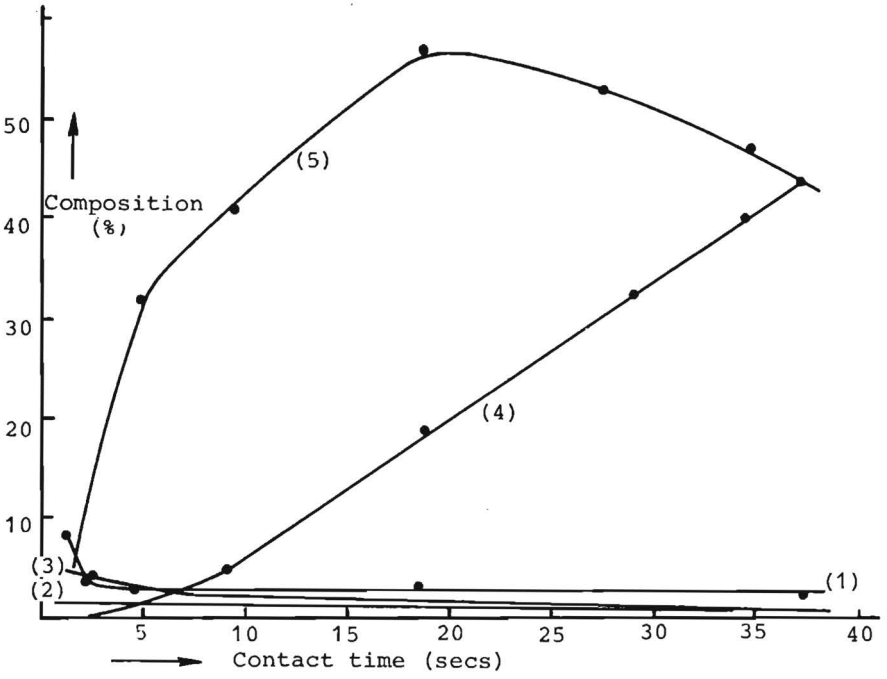


fig II-2b Thermolysis of isobornyl acetate at 445°C

(1) camphene
(2) tricyclene
(3) bornene
(4) high-boiling C_8H_{12} isomer (129°C)
(5) high-boiling C_8H_{12} isomer (126°C)

Therefore the group was isolated as such from the reaction mixture. It was shown by MS analysis that the group consisted merely of C_7H_{10} isomers with one or two C_8H_{14} compounds. Most probably the C_7H_{10} isomers consisted of dimethyl-cyclopentadienes and some derivatives with exocyclic double bonds, as was concluded from the NMR and IR spectra. The total concentration of the group increased with increasing temperatures and residence times.

Under these conditions the first small amounts of ortho-, meta- and para-xylenes also appeared. The amounts of high boiling TMCPD isomers decreased with increasing residence times. An approximate mass balance was calculated for the thermolysis of isobornyl acetate at 580°C. It turned out that the agreement between the figures (see table II-4) was as good as could be expected. In this table the concentrations of the respective components are given as functions of the residence time. No good distinction could be made between the C_8H_{14} and the C_7H_{10} isomers, since they had very similar retention times. Therefore this group was measured as a whole.

Methane and ethane might be expected to appear as side products in possibly occurring dealkylation reactions. These gases were actually found by GLC apart from ethylene.

Between 580°C and 700°C the concentrations of the high-boiling TMCPD isomers in the reaction mixture decreased further. The mass balance between xylenes and tri-methyl-cyclopentenes was, however, no longer maintained. Above 640°C only aromatics were found, including some 10% benzene. The results of the acetate thermolysis at 580°C are shown in figII-4 in which only the more important reaction products are represented. Therefore no mass balance can be deduced from these plots.

II-3-4 Thermolysis of bornyl acetate.

Bornyl acetate was thermolysed at a minimum temperature of about 445°C. A 10% conversion was obtained with a contact time of 5 secs. Only 2% camphene was formed under those conditions. The concentrations of tricyclene and bornene did not exceed 1% each. At 465°C the amounts of camphene

Table II-4

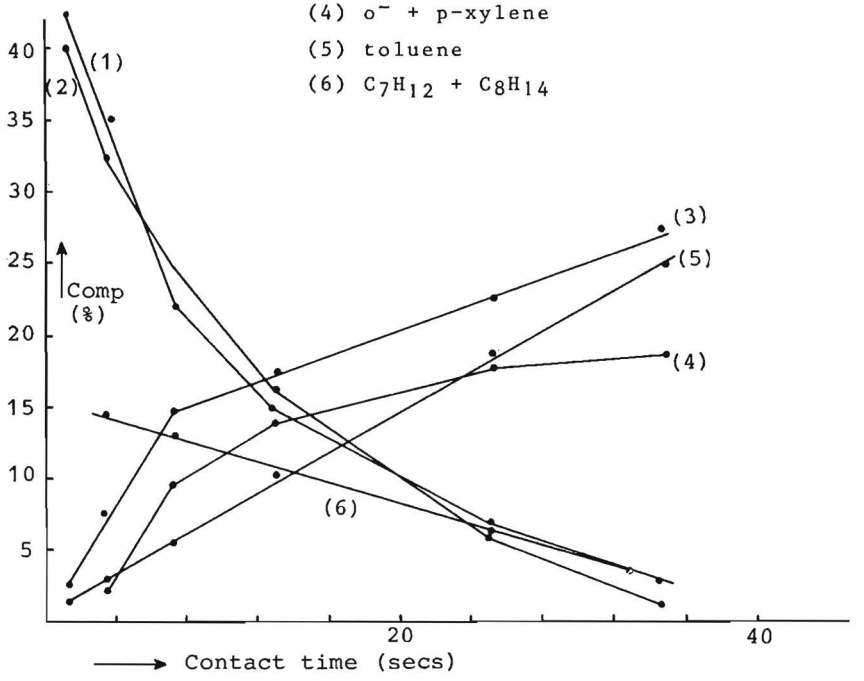
Disproportionation of high boiling TMCPD isomers at 580°C.

Change in residence times	Increase in high boiling C_8H_{12}-isomers		Decrease in Disproportion products		
9 - 18 secs.	a)	- 8.5%	o-xylene	+	4.3%
	b)	- 7.5%	m+p-xylene	+	3.2%
			toluene	+	4.8%
			$C_8H_{14}+C_7H_{10}$		3.0%
	Total	- 16.0%	Total	+	15.3%
18 - 36 secs.	a)	- 9.9%	o-xylene	+	3.1%
	b)	- 8.2%	m+p-xylene	+	5.3%
			toluene	+	8.7%
			$C_8H_{14}+C_7H_{10}$	+	- -
	Total	- 18.1%	Total	+	17.1%
36 - 72 secs.	a)	- 4.8%	o-xylene	+	3.1%
	b)	- 4.9%	m+p-xylene	+	5.9%
			toluene	+	6.8%
			$C_8H_{14}C_7H_{10}$	-	7.5%
	Total	- 9.7%	Total	+	10.7%

a) and b) refer to the TMCPD-isomers with boiling points 126°C and 129°C respectively.

fig II-4 Thermolysis of isobornyl acetate at 580°C

(1) high-boiling C_8H_{12} isomer (129°C)
(2) high-boiling C_8H_{12} isomer (126°C)
(3) m-xylene
(4) o⁻ + p-xylene
(5) toluene
(6) C_7H_{12} + C_8H_{14}



and bornene decreased from 1.5% to 0.5% each with increasing residence times (2.4 secs. to 40 secs.). At the same time tricyclene increased from 1% to 3%. These results were in fair agreement with those obtained for isobornyl acetate at the same temperature. The amounts of C_8H_{12} isomers increased from 20% to 62% for bornyl acetate and from 75% to 85% for isobornyl acetate. (residence times again between 2.4 secs. and 40 secs.). The results are shown in fig II-3. At temperature above 500°C the products of the bornyl acetate thermolysis are the same as those of the isobornyl acetate thermolysis. The relatively small discrepancies in the respective amounts of the products are caused by the smaller decomposition rate of bornyl acetate. The results of the bornyl acetate thermolysis at 580°C are given in fig II-5.

fig II-3a Thermolysis of bornyl acetate at 445°C

(1) camphene
(2) bornene
(3) high-boiling C_8H_{12} isomer (126°C)
(4) high-boiling C_8H_{12} isomer (129°C)

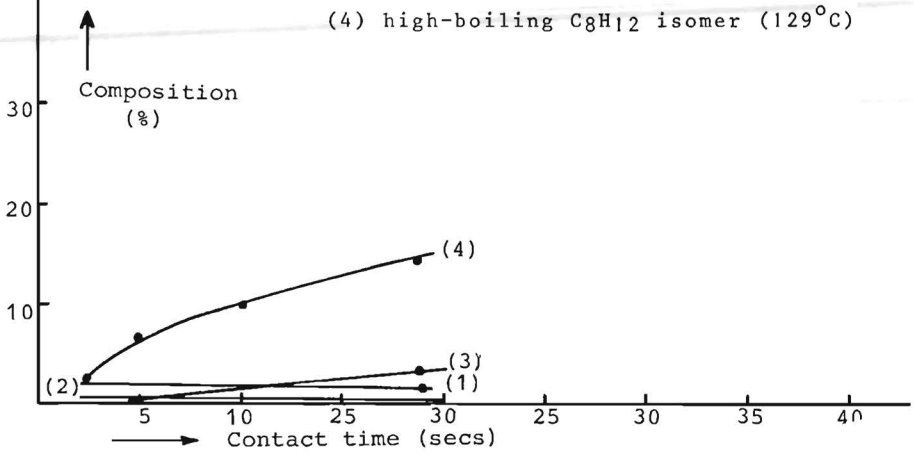


fig II-3b Thermolysis of bornyl acetate at 475°C

(1) camphene
(2) bornene
(3) high-boiling C_8H_{12} isomer (126°C)
(4) high-boiling C_8H_{12} isomer (129°C)

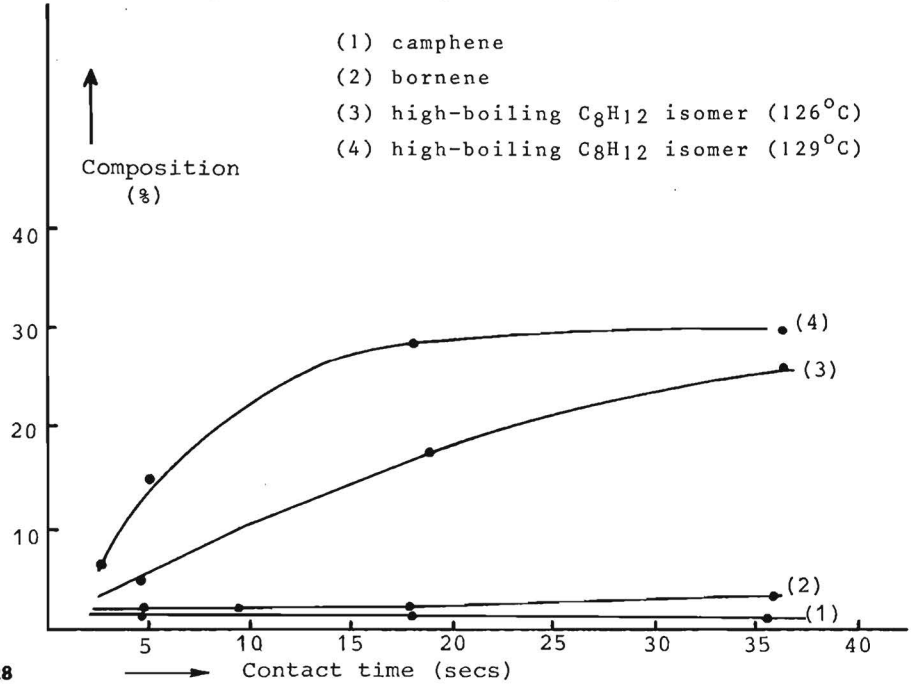
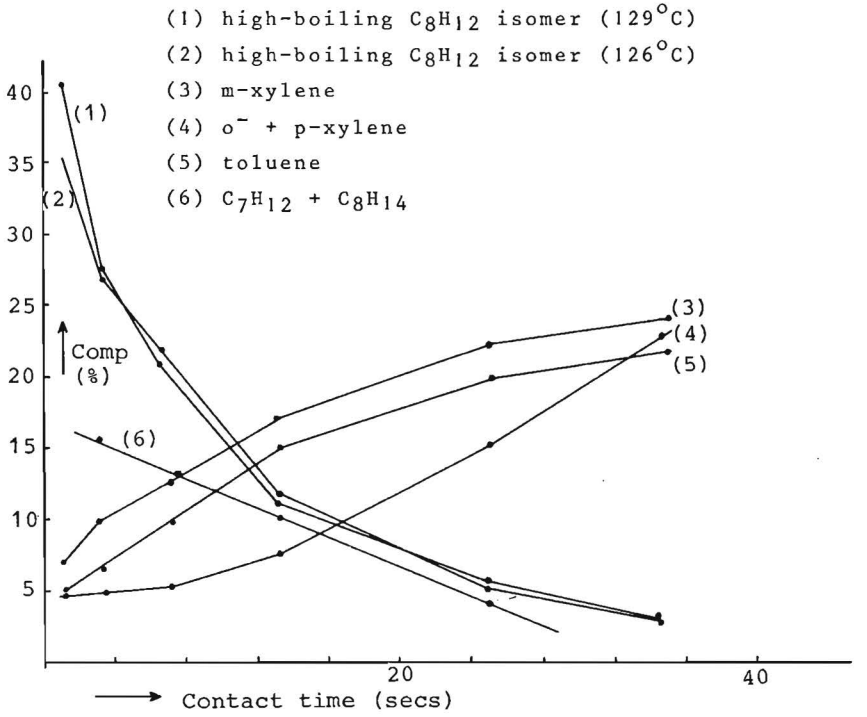


fig II-5 Thermolysis of bornyl acetate at 580°C



II-4 Discussion.

This discussion deals with the following three main subjects:

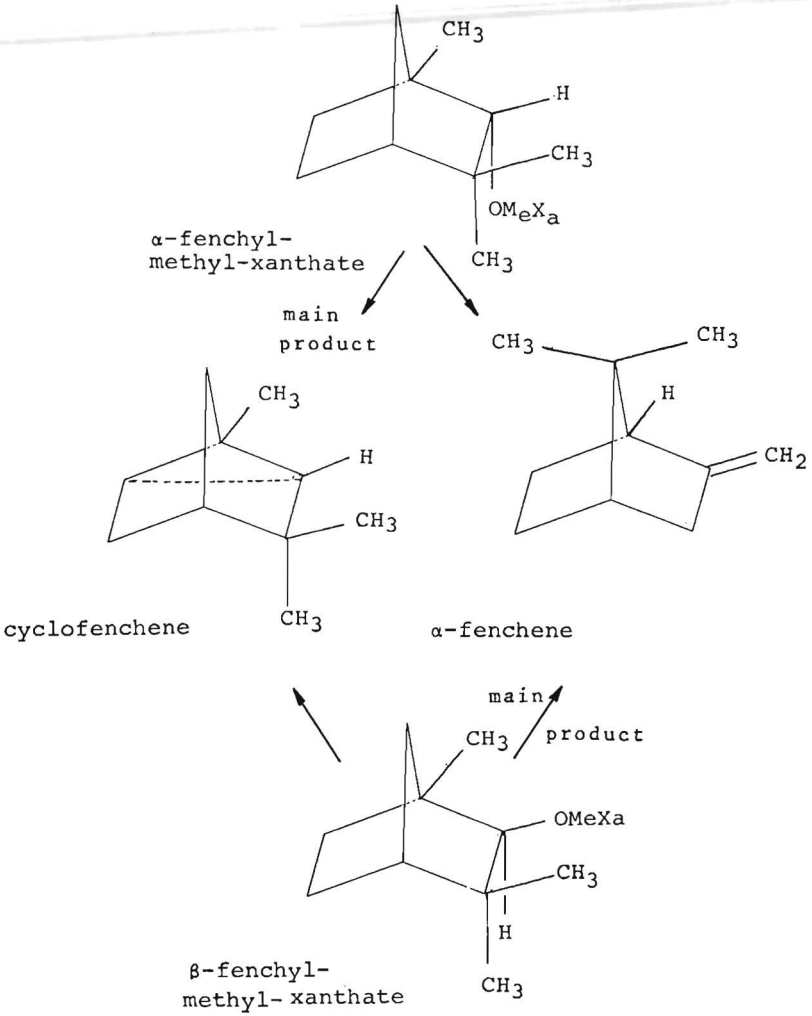
1) Conventional elimination of acetic acid.
2) Formation of hydrocarbons, smaller than $C_{10}H_{16}$.
3) Disproportion of the reaction products at high temperatures.

II-4-1 Elimination of acetic acid.

Ester thermolysis generally proceeds via elimination of the cis-β-hydrogen. These eliminations are considered to occur by a concerted, multi-centre process. This does not imply, that partial charges are not developped in the transition state. Depending upon the nature of the olefinic part as well as of the acid eliminated, the process might acquire characteristics of heterolytic processes, hence the term "quasi-heterolytic".

Decomposition of fenchyl acetate.

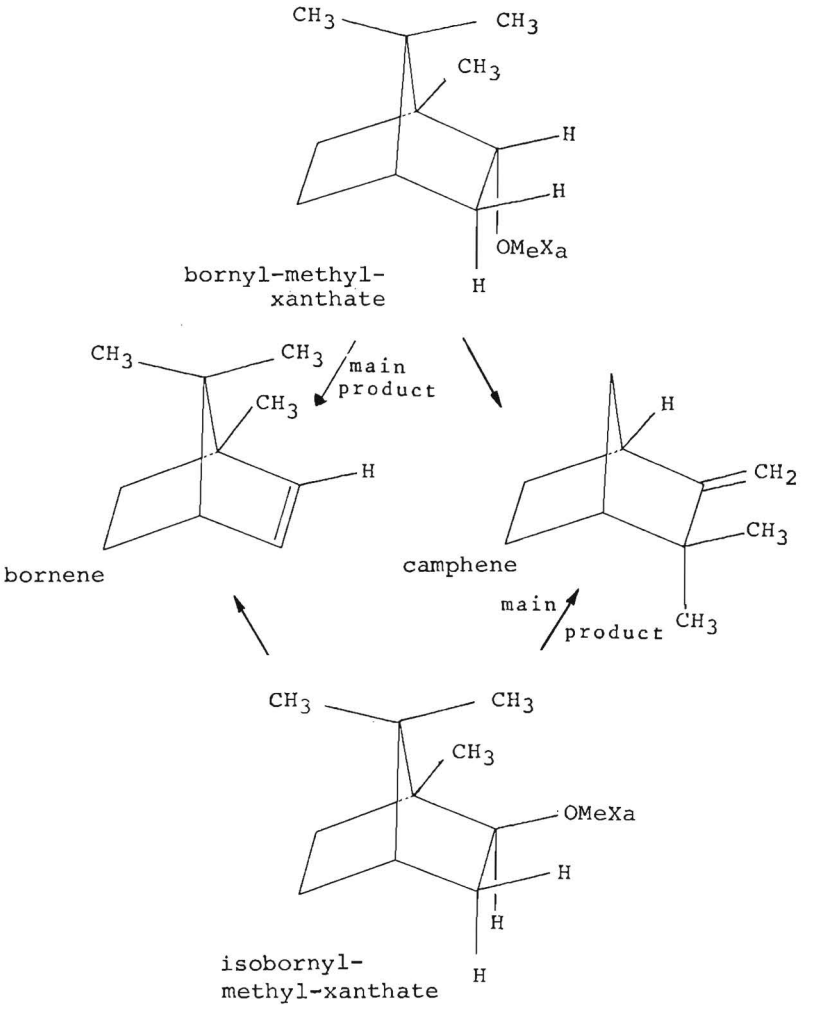
The thermal decomposition of α- and β-fenchyl-methyl-xanthates has been investigated by CHUGAEV:



Since both β-positions are occupied by methyl groups, elimination proceeds predominantly via abstraction of the 6-endo hydrogen to form cyclofenchene. The formation of α-fenchene is believed to proceed via a 7-membered transition state involving the bridgehead methyl group. Thermolysis of fenchyl acetate, as studied in this work, yields

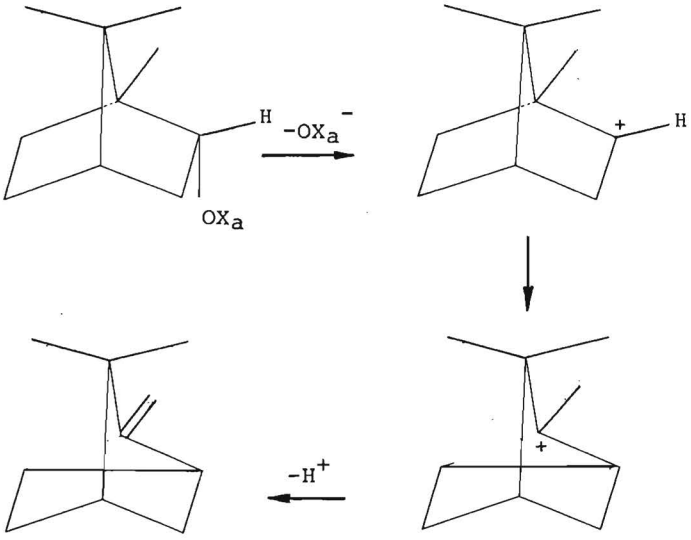
cyclofenchene with only a few percents of α-fenchene. The reaction is thus largely analogous to the methyl-xanthate decomposition.

Decomposition of bornyl- and isobornyl acetate.
The appropriate methyl xanthates have been studied by CHUGAEV (ref 13):



The main thermolysis product of bornyl-methyl-xanthate, bornene, might arise from a normal cis-β-elimination process. The camphene, formed from the isobornyl ester, possessed the same optical purity as the ester. Therefore a

concerted E_i-process with a 7-membered transition state is believed to occur, analogous to α-fenchyl-methyl-xanthate. Probably a similar mechanism is involved in the formation of camphene from norbornyl-trimethyl-ammonium salt in aqueous alkali,which has been reported by McKENNA (ref14). The camphene was of high optical purity. Pyrolysis of the same compound again yielded bornene, the normal cis-β-elimination product. The camphene, obtained from bornyl-methyl-xanthate possessed only 30% of the original optical activity. Therefore it is generally believed, that a step-wise reaction occurs in this case with a loss of asymmetry. In this reaction some charge separation occurs with the formation of carbonium ions and subsequent rearrangements of the ions:



This was clearly demonstrated by the work of BUNTON c.s. (ref 15) who investigated the thermal decomposition of bornyl- and isobornyl benzoates. Again camphene was found among the reaction products but the optical purity was low. The benzoates ionise more easily than the methyl-xanthates and therefore the camphene percentage might be higher than for the methyl-xanthates. This was actually found. The stronger the corresponding acid, the more the ionic character of the ester thermolysis will predominate.

In general the acetates ionise more easily than the benzoates. Therefore appreciable amounts of camphene might be expected from the thermolysis of bornyl- and isobornyl acetate. Actually some 30% camphene was formed in some cases (see II-3-2). The results were, however, so badly reproducible and the conditions so ill-defined that no conclusions can be drawn.
At temperatures above 430°C only ethylene and C_8H_{12}hydrocarbons or further rearrangement products are formed.It is therefore assumed that under those conditions the acetate thermolysis proceeds mainly via elimination of the cis- β-hydrogen at the 3-exo position to form bornene, which is known to undergo a retro-Diels-Alder reaction at these temperatures (see also II-4-2).

Bornyl acetate yields at 450°C only 2% camphene, the rest being decomposition products of bornene. It could not be deduced whether this is due to stereochemical or to temperature effects since isobornyl acetate at this temperature also yields decomposition products of bornene(see before).

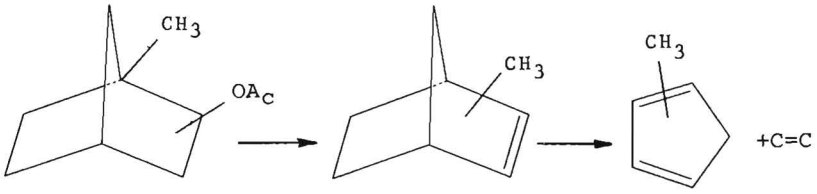
Different thermolysis rates for bornyl- and isobornyl acetate.

For a number of elimination reactions of bicyclo-(2 2 1)-heptyl systems involving carbonium ion intermediates it has been found, that the exo isomer decomposes faster than the endo isomer. How much of the observed increase in rate of decomposition of an exo derivative over that of its endo isomer is to be attributed to electronic delocalisation and how much to other factors such as differences in ground state energies, is difficult to say.
Similar, although smaller differences in reaction rates have been found for the thermolysis of a number of exo-endo ester pairs (ref 13). CHUGAEV and TOIVONEN (ref 16) found that in all cases the exo ester decomposes at the lowest temperature. The differences in decomposition temperatures ranged from 20°C to 70°C, corresponding with relative reaction rates of 4 to 130.For isobornyl- and bornyl acetate the ratio is about 7. This difference is caused largely by an entropy effect rather than by an energy effect.

It was assumed that the acetate thermolysis proceeds via a 6-membered transition state involving one of the C_3 hydrogens. It is, however, not completely clear from this picture why the endo-isomer should loose more degrees of freedom than the exo-isomer on formation of the transition state. Probably isobornyl acetate possesses a slightly lower ground state entropy as a consequence of sterical hindrance between the exo acetate group and the "cis" bridgehead methyl group. This sterical hindrance would preclude rotation of the acetate group around the C-O linkage, which connects the acetate group with the norbornane skeleton.

II-4-2 Formation of hydrocarbons, smaller than $C_{10}H_{16}$.

A firts indication that the primary hydrocarbon(s) resulting from thermolysis of bornyl- and isobornyl acetate is (are) not stable, are the results of GERMAIN and BLANCHARD (ref 17). They thermolysed 1-methyl-norbornyl acetate in a pyrex tube at 480°C and found,that the product was not the anticipated C_8H_{12} isomer 1-methyl-norbornene but a mixture of ethylene and methyl-cyclopentadiene (Me-CPD). So a retro-Diels-Alder reaction obviously occurred:



Details concerning exo/endo isomerism of the acetate and about the position of the methyl group in the resulting CPD ring are not given. Most probably, however a mixture of 1-Me-CPD and 2-Me-CPD was formed(see also chapter III). In a similar way bornene has been shown to give 1.5.5.-tri-methyl-cyclopentadiene (1.5.5.-TMCPD) and ethylene. (ref 18). The thermolysis results, as described in II-3-3 however indicate that two TMCPD's vis. 1.5.5.-TMCPD and 2.5.5.-TMCPD are initially formed and that they convert to two other isomers vis. 1.2.4.-TMCPD and 1.2.3.-TMCPD. This

conversion as well as its mechanism, is dealt with separately in chapter III. Here the formation of 1.5.5.-TMCPD and 2.5.5.-TMCPD is discussed.

Separate thermolysis of the various $C_{10}H_{16}$ hydrocarbons: camphene, tricyclene and bornene showed, that the last compound yielded at 320°C 1.5.5.-TMCPD and a few percents of 2.5.5.-TMCPD (together with "secondary" 1.2.4.-TMCPD and 1.2.3.-TMCPD).
The formation of the 1.5.5.-isomer undoubtedly involves a retro-Diels-Alder reaction of bornene. The rate constants for the reaction of norbornene to cyclopentadiene and ethylene has recently been studied over a wide temperature range (ref 19). The remaining question is the formation of 2.5.5.-TMCPD. The source of 2.5.5.-TMCPD might be ξ-fenchene. Thermolysis of this compound gave, in addition to ethylene indeed 2.5.5.-TMCPD. Moreover, a small amount of 1.5.5.-TMCPD was also present. Thus the complementary observations:

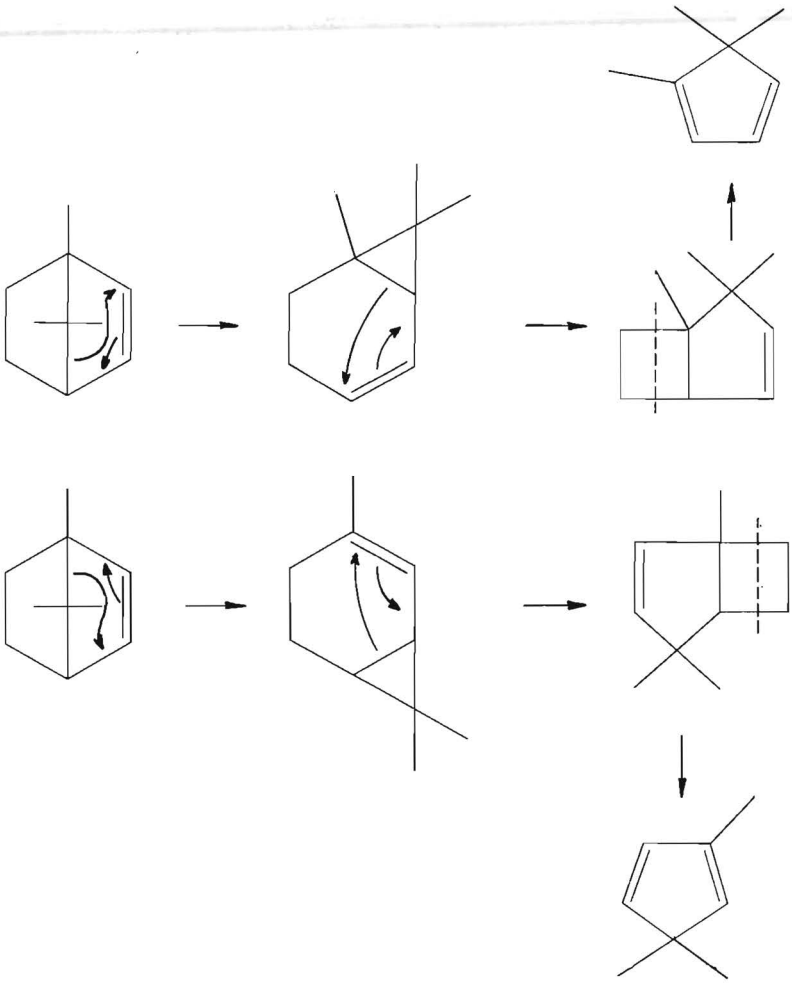
bornene → mainly 1.5.5.-TMCPD + some 2.5.5.-TMCPD

and: ξ-fenchene → mainly 2.5.5.-TMCPD + some 1.5.5.-TMCPD

have to be explained.

An interconversion of 1.5.5.-TMCPD and 2.5.5.-TMCPD under the reaction conditions was definitely ruled out (see chapter III). An interconversion of bornene and ξ-fenchene has to be considered. A superfically analogous isomerisation has been observed by ALDER and ACHE (ref20). They found, that heating of either 1-me-norbornene or 2-me-norbornene in closed vessels at 180°C for several hours yielded the other isomer (both isomers are ultimately converted to 2-exo-methylene-norbornane). However this reaction might result from a retro-Diels-Alder reaction of the 1-isomer to ethylene and 1-me-CPD, isomerisation of 1-me-CPD to 2-me-CPD, followed by a Diels-Alder reaction. Comparison of the reaction conditions with the known rates for each of the processes lends high probability to this route. Hence, ALDER and ACHE's results do not constitute any evidence for an isomerisation of bornene to ξ -fenchene. (Note that the isomerisation of 1-me-CPD to 2-me-CPD is a very fast reaction, involving the shift of hydrogen, see chapter III).

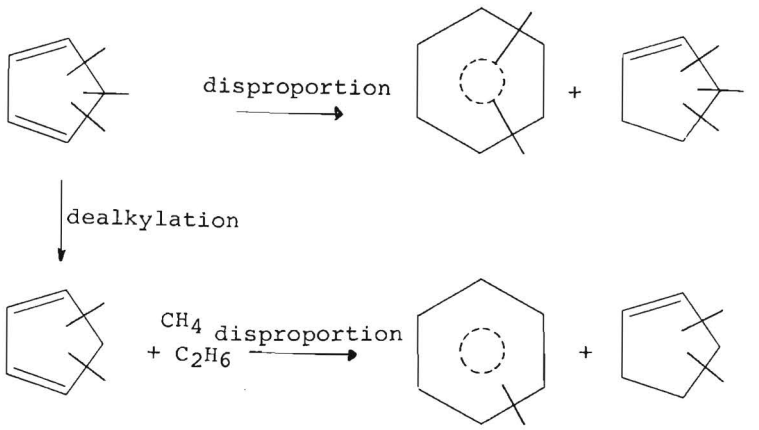
An alternative route for the formation of the C_8H_{12} hydrocarbons from the initially formed terpenes would be the occurrence of bicyclo-(320)-heptene-2 intermediates:



This mechanism does not explain why mainly 1.5.5.-TMCPD is formed from bornene and 2.5.5.-TMCPD from ξ-fenchene. Therefore it is assumed that the above scheme represents only a part of the total reaction mechanism, the main decomposition products being formed via the "normal" retro-Diels-Alder reaction.

II-4-3 Disproportion of the high-boiling C_8H_{12}-isomers.

It was shown that also C_8H_{14} and C_7H_{10}-isomers, toluene and the three xylenes were found among the reaction products apart from high-boiling C_8H_{12}-isomers at thermolysis between 500°C and 600°C. An approximate mass balance was calculated from which it was evident, that the reactions in this temperature range might be summarised by the scheme:



Methane and ethane might be expected to appear as side-products in the dealkylation reactions. Actually these gasses were found by GLC in the appropriate amounts apart from ethylene, resulting from the retro-Diels-Alder reactions. At temperatures above 600°C only aromatics and methane/ethane were found.

CHAPTER III

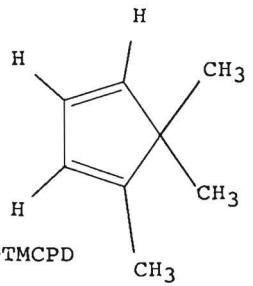
ISOLATION AND THERMAL BEHAVIOUR OF SOME TRI-METHYLCYCLOPENTADIENES

III-1 Introduction

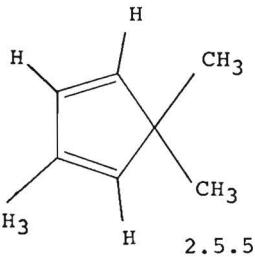
In chapter II it has been shown, that in the reaction product, obtained by thermolysing bornyl- and isobornyl acetate there are 4 predominant components which can be distinguished into 2 low boiling components and 2 high boiling ones. By changing temperature and residence time the relative amounts of these components change as well; under more severe reaction conditions the two low boiling components are converted into the high boiling ones(seeII-3-3).

It was suspected that all of them are tri-methyl-cyclopenta-1,3-dienes (TMCPD's), the former being the two possible isomers with geminal methyl groups (1.5.5.-TMCPD and 2.5.5.-TMCPD). All these suspicions were confirmed.

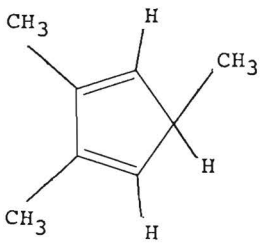
In the first part of this chapter the isolation of the various tri-methyl-cyclopentadienes is described. The proves for the structure assignments will be given in chapter IV:



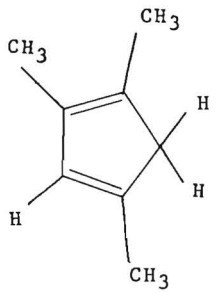
1.5.5.-TMCPD



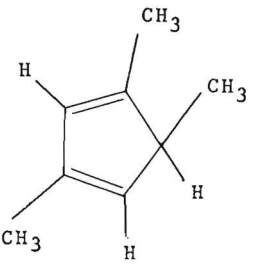
2.5.5.-TMCPD



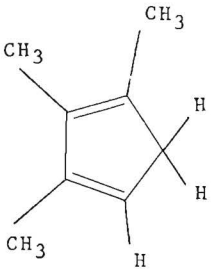
2.3.5.-TMCPD



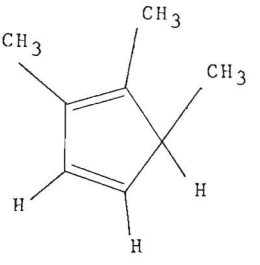
1.2.4.-TMCPD



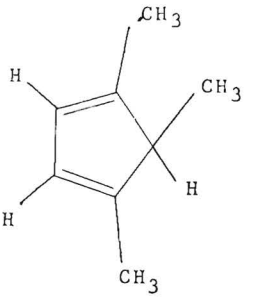
1.3.5.-TMCPD



1.2.3.-TMCPD

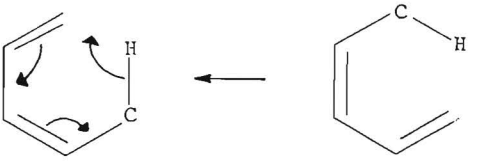


1.2.5.-TMCPD

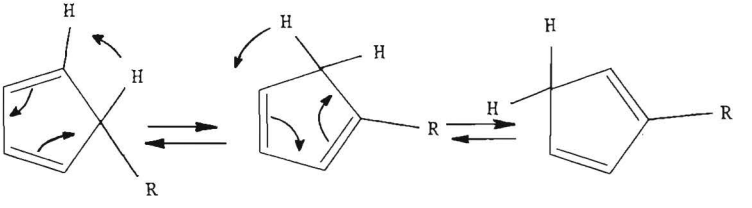


1.4.5.-TMCPD

In the second part of this chapter the thermal behaviour of the tri-methyl-cyclopentadienes is described together with additional experiments to elucidate the nature of the process involved in the observed rearrangements.These investigations were undertaken for the following reasons:
In recent years a number of intramolecular thermal 1⟶5 shifts of hydrogen atoms in hydrocarbons, containing a pentadienylic system have been discovered (refs 21,22):



In 1963 MIRONOV and ROTH (refs 23,24) independently proved the occurence of such processes in cyclopentadiene and simple derivatives:



The interconversions:

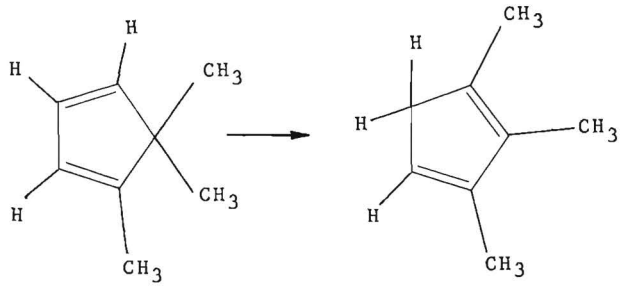
1.2.3.-TMCPD ⇄ 1.2.5.-TMCPD ⇄ 1.4.5.-TMCPD

and · 2.3.5.-TMCPD ⇄ 1.2.4.-TMCPD ⇄ 1.2.5.-TMCPD

involve such a process. The reactions are relatively fast, the half lives at room temperature being of the order of a few hours.

The question arises whether atoms or groups other than hydrogen, in particular methyl, can also shift intramolecularly. Methyl substituted cyclopentadienes seem very suitable sytems to test this hypothesis.
The possibility of such a rearrangement was suggested by a few literature data. ALDER and MUDERS decarboxylated β - camphylic acid and assigned the structure 1.5.5.-TMCPD to the resulting hydrocarbon. (ref 25).
Previously DAMSKY (ref 26) thermolysed a mixture of calcium camphylate and sodium oxyde under more drastic conditions and obtained a hydrocarbon which the author thought to be 1.5.5.-TMCPD. More recently ALDER and MUDERS repeated DAMSKY's experiments and assigned the structure 1.2.3.-TMCPD to the product. (ref 39).

We believe the assignments of ALDER and MUDERS to be correct, although on the base of present day knowledge the 1.2.3.-isomer very likely contained some of its H-shift isomers 1.4.5.-TMCPD and 1.2.5.-TMCPD. Moreover ALDER and MUDERS under less-defined conditions observed at 400° C the isomerisation of 1.5.5.-TMCPD to 1.2.3.-TMCPD:



In 1963 MIRONOV c.s. in a footnote suggested that this reaction might involve an intramolecular methyl shift(ref23).

III-2 Experimental and results.

III-2-1 Isolation of the trimethyl-cyclopentadienes.
Isobornyl acetate was thermolysed at 470°C in the macroreactor described in II-2-2. The residence time was about
 12 secs. Under these conditions a hydrocarbon mixture was

isolated, containing approximately:

1%	2.5.5.-TMCPD
5%	1.5.5.-TMCPD
35%	1.2.4.-TMCPD + H-shift isomers
35%	1.2.3.-TMCPD + H-shift isomers
24%	dealkylation- and degradation products.

This mixture was distilled at atm pressure in a spinning band column with a reflux ratio of 1:20 until a top temperature of 110°C was reached. The fractions up to that temperature contained the lower boiling dealkylation products together with the major part of 2.5.5.-TMCPD and 1.5.5.-TMCPD.

These fractions (2.5 ml aliquotes) were subjected to preparative GLC, using a 7 m, 30 mm ID column, which was packed with Apiezon-L on Sterchamol.The column temperature was 95°C. Helium or a nitrogen mixture was used as a carrier gas at a flow rate of 150 ml/min.Under these conditions the retention times of 2.5.5.-TMCPD and 1.5.5.-TMCPD are 70 mins and 85 mins respectively. The compounds were collected in a trap, kept at- 30°C. A typical chromatogram is shown in fig. III-1.

Unfortunately pure compounds could not be isolated from the distillate in this manner. As a consequence of the similar boiling points and retention times a few percent of 1.5.5.-TMCPD were always present in 2.5.5.-TMCPD and vice versa (see fig. III-2). Moreover,GLC on an analytical column showed that 2.5.5.-TMCPD and 1.5.5.-TMCPD were each contaminated with a compound (d and c resp. in fig.III-2) which was absent in the original fractions. Since they are not present in the preparative chromatograms these compounds are probably formed continously from 2.5.5.-TMCPD and 1.5.5.-TMCPD respectively in the preparative column. Very likely the Sterchamol support promoted these reactions.

The analytical GLC was performed with a different support material (Gaschrom) while the temperature was 80°C. The retention times were 2.6 and 3.0 mins respectively. The influence of the support material was demonstrated clearly by re-injecting one of the collected portions of "pure"

fig III-1

Preparative chromatogram of 1 ml sample of distillate up to 110°C. The little arrows in the figure indicate the limits between which the various compounds were trapped.

a) 1+2- mono me - C.P.D. (mixture)
b) 2.5.5.-TMCPD
c) 1.5.5.-TMCPD

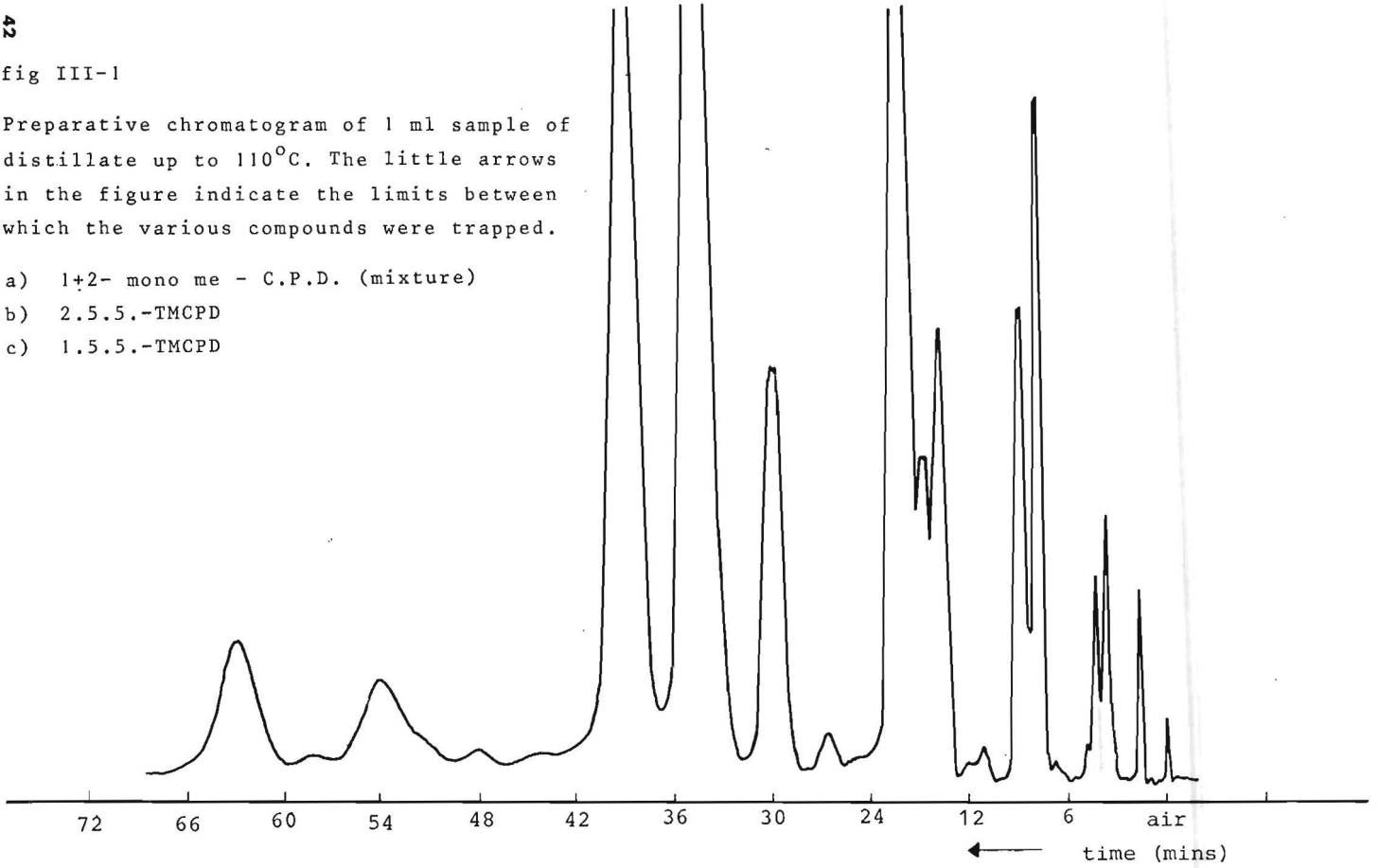


fig III-2

Chromatograms on 4m analystical Apiezon column of:

A) purified 2.5.5.-TMCPD

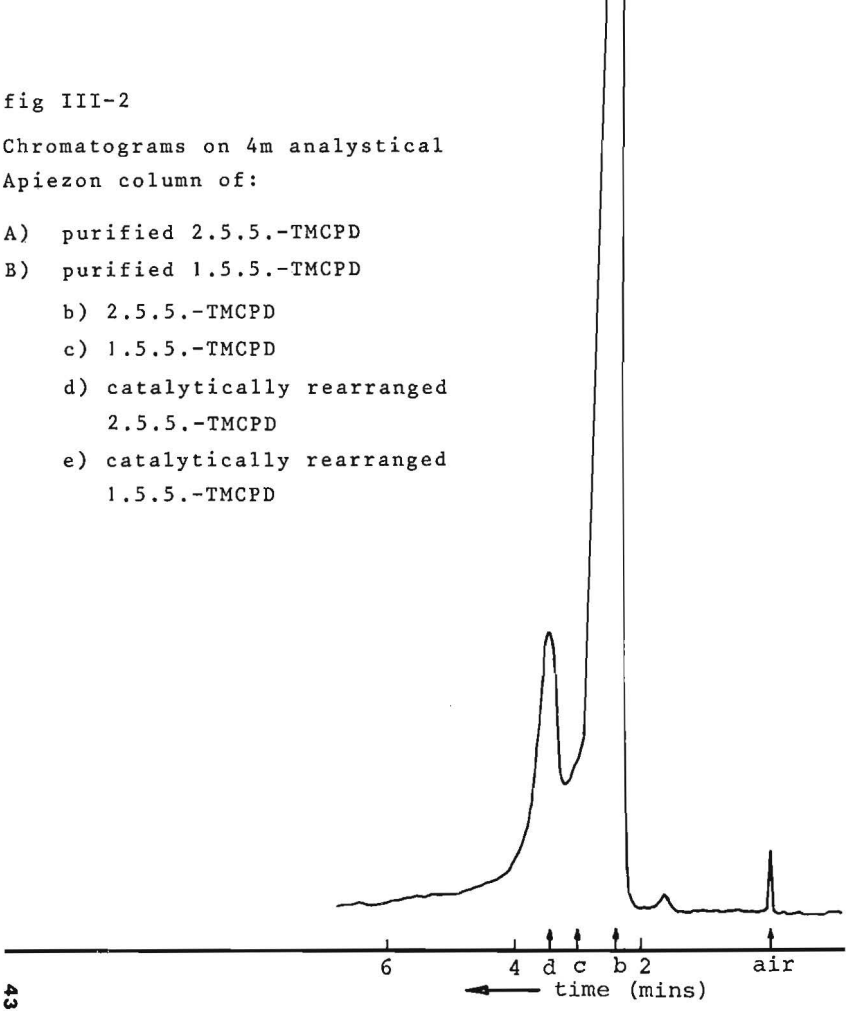
B) purified 1.5.5.-TMCPD

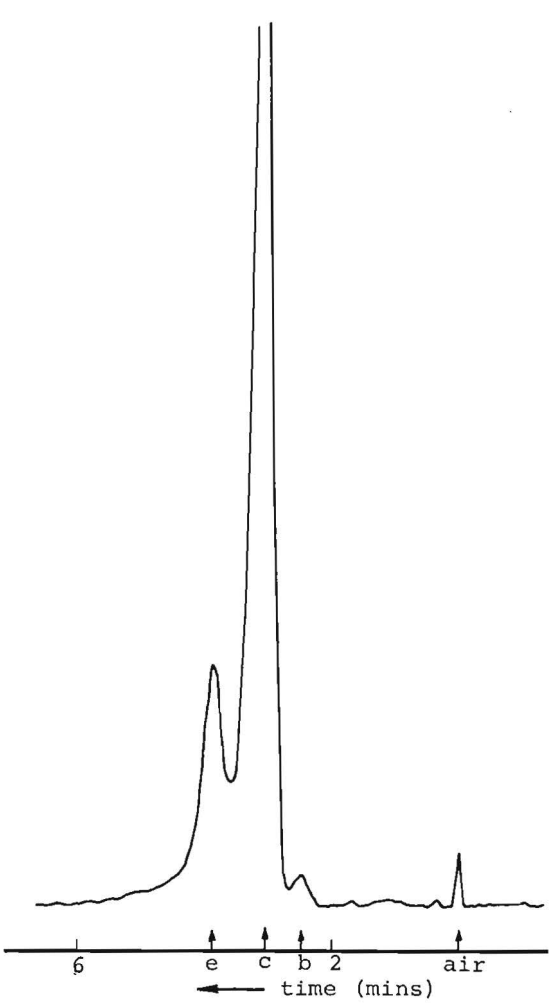
b) 2.5.5.-TMCPD

c) 1.5.5.-TMCPD

d) catalytically rearranged 2.5.5.-TMCPD

e) catalytically rearranged 1.5.5.-TMCPD





1.5.5.-TMCPD. After the second run the percentage of the decomposition product had grown considerably.
Fortunately the two contaminants showed a remarkable thermal stability so that they were of no influence in the isomerisation experiments. The structures of the two impurities will be discussed in chapter IV. They will be referred to as exocyclic double bond isomers.

The original distillation residue yielded only fractions of almost constant composition on careful distillation. (see fig.III-3). They contained about 75% of 1.2.4.-TMCPD, the rest being 1.2.3.-TMCPD and H-shift isomers of both 1.2.4.-TMCPD and 1.2.3.-TMCPD.The concentration of 1.2.4.-TMCPD was raised to about 97% by preparative GLC. The three TMCPD isomers, thus obtained, were stored at a temperature, lower than 100°C.

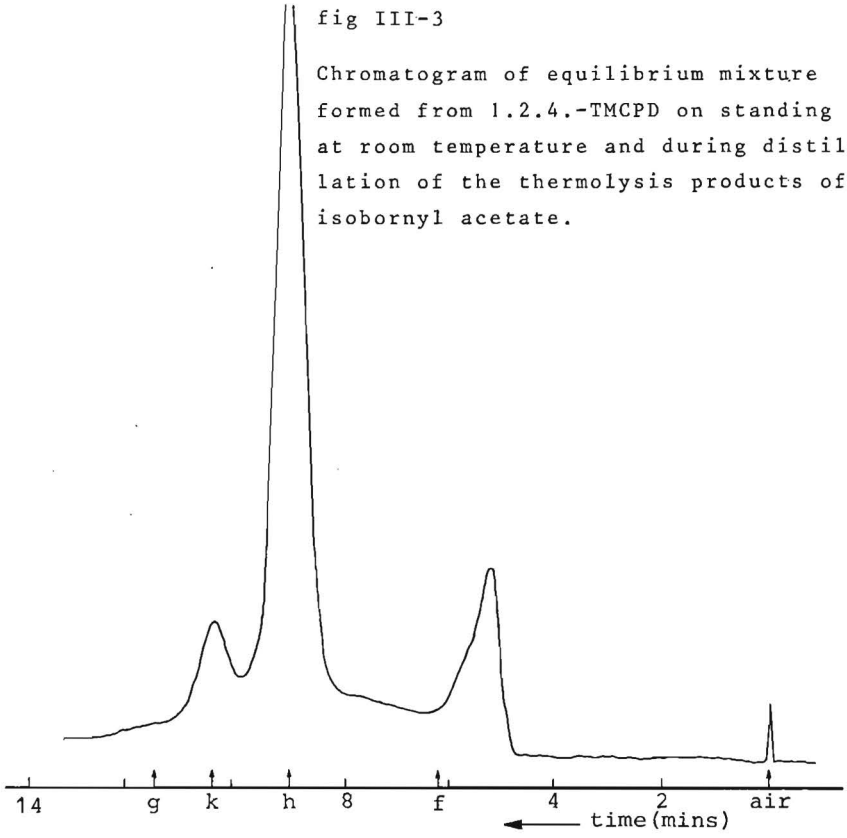


fig III-3

Chromatogram of equilibrium mixture formed from 1.2.4.-TMCPD on standing at room temperature and during distillation of the thermolysis products of isobornyl acetate.

On standing at room temperature, (97% pure) 1.2.4.-TMCPD slowly rearranged to form a mixture with the same composition as the distillation fractions. This process is accelerated by heating (see fig.III-3).
1.2.3.-TMCPD could not be purified in the way described above since it isomerised partially during preparative gaschromatography to a higher boiling compound, the structure of which will be discussed in chapter IV. Therefore a different approach was taken; isobornyl acetate was thermolysed during 6 secs. at 420°C (instead of during 12 secs. at 470°C). Under these conditions the hydrocarbon mixture contained mainly 1.2.3.-TMCPD and some 20% 1.2.4.-TMCPD (see fig.III-4; see II-3). The hydrocarbons were carefully distilled off under reduced pressure (30 mm Hg) at 40-50°C. The distillate was purified further on the analytical column by repeated injection of 8 µl samples. The final purity was estimated by GLC at about 95%.

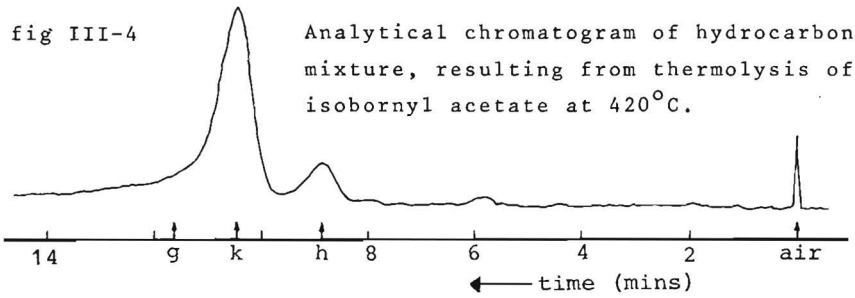


fig III-4 Analytical chromatogram of hydrocarbon mixture, resulting from thermolysis of isobornyl acetate at 420°C.

III-2-2 Ampoule experiments.

a) Isomerisation and polymerisation of 2.5.5.-TMCPD and 1.5.5.-TMCPD.

500 Microliter portions of 2.5.5.-TMCPD and of 1.5.5.-TMCPD were sealed in glass ampoules which were heated at 320°C for ½hr. The resulting C_8H_{12} fractions were transferred from the ampoule by vacuum distillation.
It was shown subsequently by GLC (4m Apiezon at 80°C) that the following isomerisation reactions had occurred:

2.5.5.-TMCPD ⟶ 1.2.4.-TMCPD + 1.2.3.-TMCPD
1.5.5.-TMCPD ⟶ 1.2.3.-TMCPD

This was substantiated further by spectroscopic methods. The most convincing evidence was obtained from the NMR

spectra, since it was shown unambiguously, that heating of the two geminally substituted isomers resulted in a shift of all methyl groups to double bond positions. IR spectrometry was used mainly to distinguish between 1.2.4.-TMCPD and 1.2.3.-TMCPD. A more detailed description of the spectra will be given in chapter IV.

A considerable polymerisation was observed during both isomerisation experiments. A series of reference experiments was performed at 265°C for 2.5.5.-TMCPD and 1.5.5.-TMCPD and isomerisation products with hexane and decane as internal standards. In this way an estimate could be made of the extent of polymerisation during the isomerisation reactions, see table III-I.

Table III-1

Polymerisation of 2.5.5.- TMCPD, 1.5.5.-TMCPD and their isomerisation products at 265°C.

Time (hrs)	½	2	5½	11	16
%polymer. 2.5.5.-TMCPD	3	6	10	17	20
%polymer. 1.5.5.-TMCPD	9	40	72	81	85

b) Isomerisation and disproportionation of 1.2.3.-TMCPD.

Some interesting thermal experiments were performed with 1.2.3.-TMCPD between 100°C and 185°C. It turned out that 1.2.3.-TMCPD isomerises to the same higher boiling compound which is found during purification of 1.2.3.-TMCPD by preparative GLC (see also III-2-I). Some quantitative results are summarised in table III-2.

Table III-2

Thermal isomerisation of 1.2.3.-TMCPD between 100°C and 185°C in glass ampoules.

Temp (°C)	-	100	100	155	155	185	185	185
Heating time (hrs)	0	3	6	3	6	3	6	9
% Isomerisation	4	6	11	14	17	18	18[5]	19

Heating at 320°C yielded a mixture, containing one major component, which was shown to be 1.2.3.-tri-methyl-cyclopentene (laurolene) by IR and NMR spectrometry.

Heating for ½hr at 420°C resulted in the formation of a

mixture of degradation and disproportionation products. Most of them are still unidentified, a number are indentical with compounds, obtained by thermolysis of isobornyl acetate at 520°C. (see also II-3-3).

c) Heating and disproportionation of 1.2.4.-TMCPD

After heating 1.2.4.-TMCPD at 210°C for 1 hr a mixture is formed with the same composition as that, which is obtained during purification of 1.2.4.-TMCPD by preparative GLC (see also III-2-1). Heating at 320°C and at 420°C (½ hr) yields again the same mixture as that, which is obtained from 1.2.3.-TMCPD (see before). Presumably the disproportionation of 1.2.3.-TMCPD proceeds via the formation of 1.2.4.-TMCPD.

A draw-back of the ampoule method is that it generally demands long reaction times in order to avoid too large errors caused by the warming up and cooling down periods. As a consequence of the long reaction times rather low temperatures have to be applied at which as a rule the bimolecular Diels Alder addition competes strongly with the isomerisation processes. This makes the method less suitable for obtaining quantitative results. The ampoule method however provides a convenient means of obtaining samples large enough to enable spectroscopic methods to be applied before and after the isomerisation reactions. The results obtained are largely qualitative.Quantitative results were obtained using the micro-reactor method (see III-3-2).

III-2-3 Micro-reactor results

a) General

The microreactor has been described in detail in section II-2-3. The analyses were carried out by GLC on a 30m, squalane coated capillary column at 70°C. The resolution was sufficient for separate integration of the various peaks.

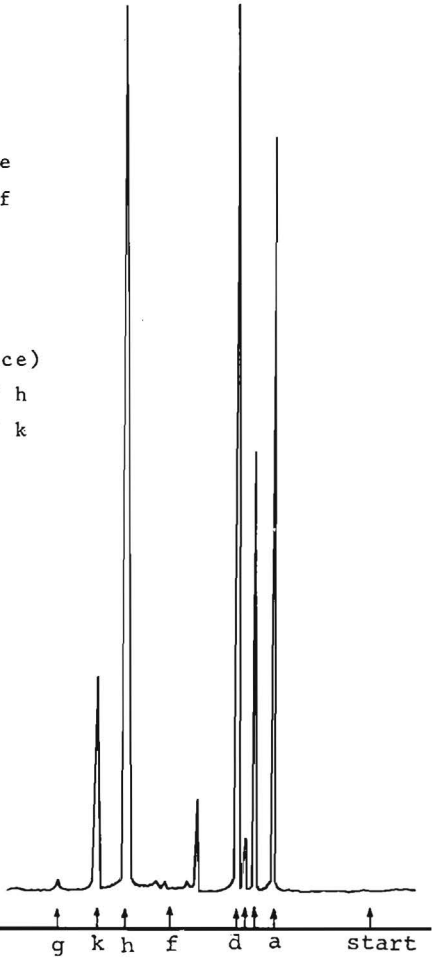
When 2.5.5.-TMCPD was injected into the microreactor, the chromatogram clearly showed 1.2.4.-TMCPD and 1.2.3.-TMCPD to be the primary products. A chromatogram is reproduced in fig. III-5. It further appears that under these conditions the impurity present in the starting material remains

unchanged (peak d in fig. III-5). Similarly 1.5.5.-TMCPD gave only 1.2.3.-TMCPD as the primary product.
At temperatures above 350°C 1.2.4.-TMCPD rearranged further to a large number of unindentified products. These compounds are represented by the minor peaks in the chromatograms (f). In the reaction rate calculations the quantities of secondary products were added to those of the appropriate primary products. 1.2.3.-TMCPD was isomerised to an exocyclic double bond derivative mentioned already in III-3-1-b. (g in the chromatogram of fig. III-5).
It was shown further that no measurable quantities of 1.2.3.-TMCPD were formed from 1.2.4.-TMCPD and vice versa at temperatures below 380°C. Therefore it was assumed, that all 1.2.3.-TMCPD observed at the isomerisation of 2.5.5.-TMCPD was formed as a "primary" product. The isomerisation

fig III-5

Capillary chromatogram of the microreactor isomerisation of 2.5.5.-TMCPD to 1.2.4.-TMCPD and 1.2.3.-TMCPD

b,c.d see fig III-2
a) benzene (indernal reference)
f) rearrangement products of h
g) rearrangement products of k
h) 1.2.4.-TMCPD
k) 1.2.3.-TMCPD



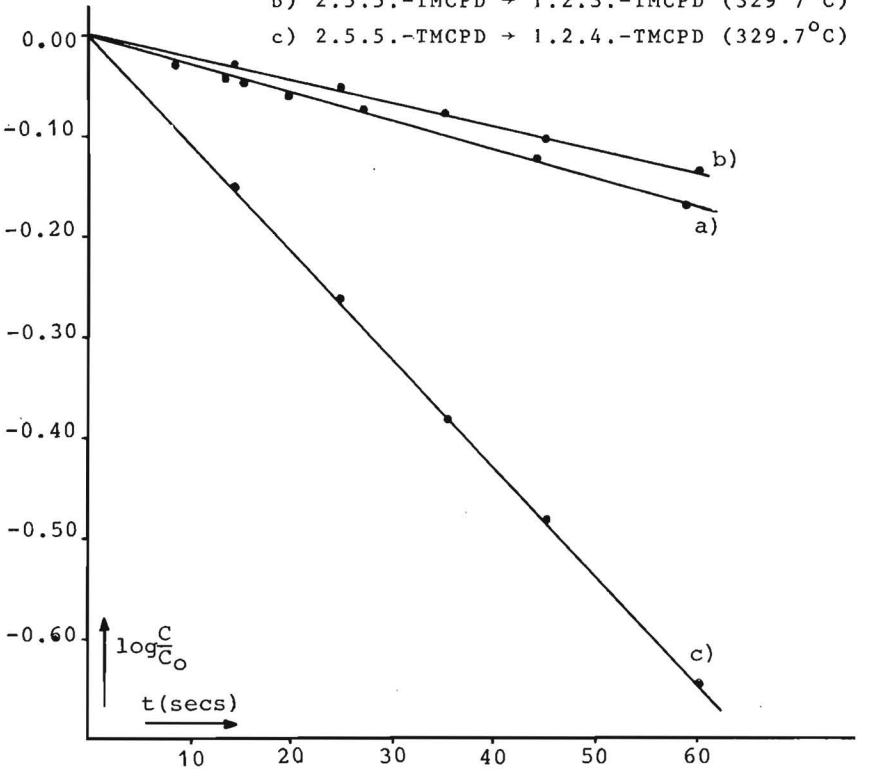
of 1.5.5.-TMCPD was carried out between 350°C and 400°C so that in the last part of the temperature range some secondary effects may be expected.
The isomerisation: 1.2.4.-TMCPD ⟶ 1.2.3.-TMCPD involved some special difficulties. "Pure" 1.2.3.-TMCPD contained a few percents of 1.2.4.-TMCPD and vice versa. Further both isomers underwent side-reactions at 400°C(see above). For those reasons the thermodynamic quantities for this equilibrium have not been determined. The reaction was only studied in a qualitative way.

b) Order of the isomerisation reactions.

The decrease in concentrations of 1.5.5.-TMCPD and 2.5.5.-TMCPD were measured as functions of the residence times at constant temperatures (329.7°C and 370.6°C respectively). In fig. III-6 the values of the conversions are plotted

fig III-6 First-order plots of the isomerisation reactions:

a) 1.5.5.-TMCPD → 1.2.3.-TMCPD (370.6°C)
b) 2.5.5.-TMCPD → 1.2.3.-TMCPD (329 7°C)
c) 2.5.5.-TMCPD → 1.2.4.-TMCPD (329.7°C)



against time on a semi-logarithmic scale. Two straight lines are obtained, showing that both reactions are of 1st order.

For the reaction:

$$1.5.5.\text{-TMCPD} \xrightarrow{k_3} 1.2.3.\text{-TMCPD}$$

the value of k_3 could be determined directly from the line. For the reactions:

$$2.5.5.\text{-TMCPD} \xrightarrow{k_1} 1.2.4.\text{-TMCPD}$$

$$2.5.5.\text{-TMCPD} \xrightarrow{k_2} 1.2.3.\text{-TMCPD}$$

only a total k ($k_1 + k_2$) was obtained in this way. The values of k_1 and k_2 were evaluated from the relative amounts of 1.2.4.-TMCPD and 1.2.3.-TMCPD in the reaction product.

c) Activation quantities.

Subsequently the values of k were determined at different temperatures. The results are given in figs. III-7 and

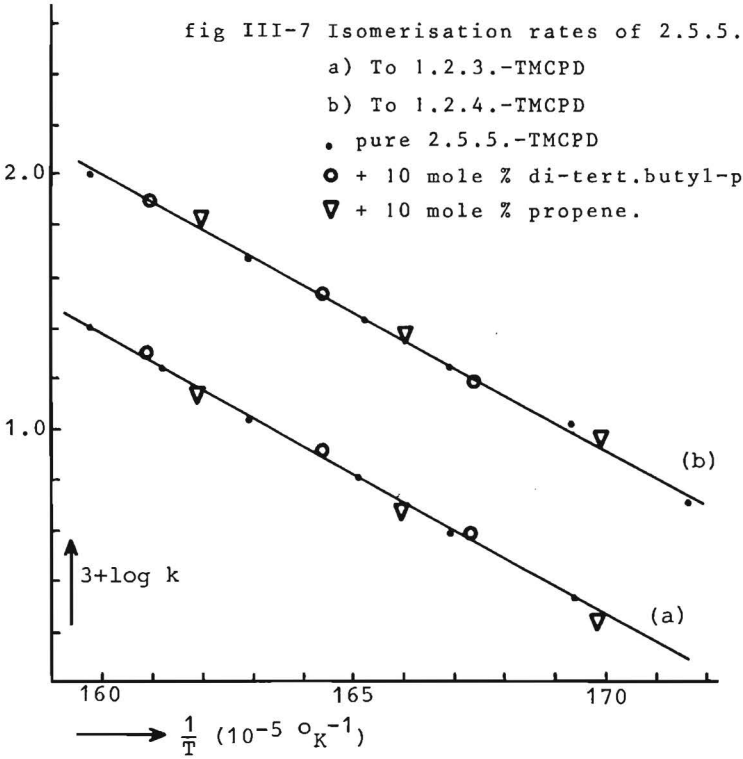


fig III-7 Isomerisation rates of 2.5.5.-TMCPD
a) To 1.2.3.-TMCPD
b) To 1.2.4.-TMCPD
• pure 2.5.5.-TMCPD
o + 10 mole % di-tert.butyl-peroxyde
▽ + 10 mole % propene.

III-8. The activation quantities given in table III-3 were calculated from the experimental data by means of the least square fit.

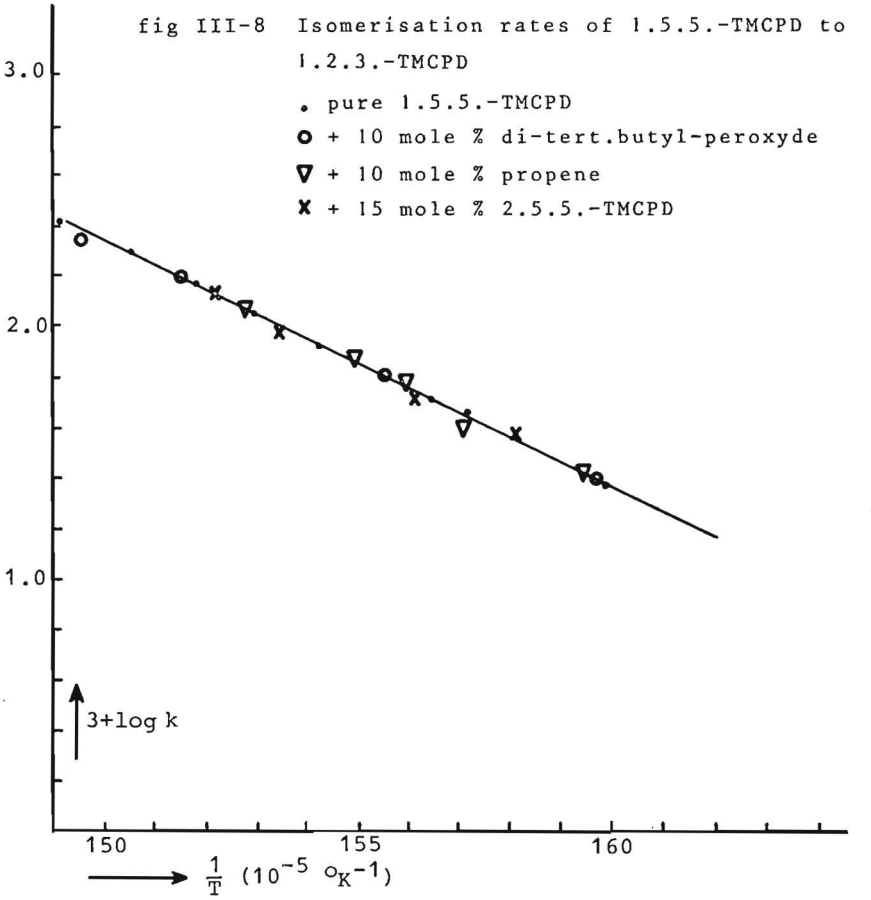


fig III-8 Isomerisation rates of 1.5.5.-TMCPD to 1.2.3.-TMCPD

- pure 1.5.5.-TMCPD
- + 10 mole % di-tert.butyl-peroxyde
- + 10 mole % propene
- + 15 mole % 2.5.5.-TMCPD

Table III-3 Activation quantities

Reaction	^{10}logA	E (kcal/mole)	H (kcal/mole	s^{cal}/ degr. mole
2.5.5 ⟶ 1.2.4.	13.88	45.4	44.2	+ 6
2.5.5 ⟶ 1.2.3.	14.39	45.6	44.4	+ 3
1.5.5 ⟶ 1.2.3.	14.62	41.6	40.3	- 1

d) Addition of radical starters and inhibitors.

The conversion of 1.5.5.-TMCPD was not influenced by the addition of 15% of 2.5.5.-TMCPD, which isomerises about 5

times as fast as 1.5.5.-TMCPD. The derived rate constants are in complete agreement with those for the isomerisation of pure 1.5.5.-TMCPD (see fig. III-8).
For both 2.5.5.-TMCPD and 1.5.5.-TMCPD a series of reaction rate measurements were performed at three different temperatures for the pure samples as well as after addition of the radical starter di-tert.butyl-peroxyde (about 10 mole %). At each temperature the rate constants were determined at three different reaction times. The results, given in figs. III-7 and III-8, show that the presence of the peroxyde does not affect the rates of the reactions.

An interesting side effect was noticed. In all previous experiments the derivatives with exocyclic double bonds appearing as impurities in 1.5.5.-TMCPD and 2.5.5.-TMCPD after purification by preparative gaschromatography (see III-2-1) showed a remarkable thermal stability. In the presence of di-tert.butyl-peroxyde, however, these isomers disappeared gradually. In the chromatograms a few higher boiling compounds were observed. They could arise from a combination of the exocyclic double bond isomer with one or more methyl radicals.
The influence of a radical inhibitor was also investigated by carrying out the reactions in the presence of propene. The reactant and propene were premixed in the following way: A 50 cc glass flask was equipped with a rubber injection piece. After evacuation approximately 30 µl liquid 2.5.5.-TMCPD or 1.5.5.-TMCPD were introduced which evaporated at once. About 10 mole % of propene gas was added. 50 µl gas mixture samples were introduced into the reactor. This small quantity required the highest detector sensitivity for analysis.
To avoid complications arising from a comparison of results obtained by different methods, each time two series of experiments were performed using the gas sampling technique, one with addition of propene and a second "reference experiment" without propene. The results are shown again in figs. III-7 and III-8.
This gas sampling technique has an advantage. When using liquid samples always some dimers are present as well,

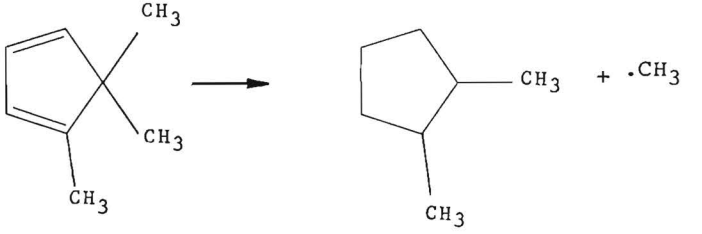
which are monomerised in the reactor into the corresponding TMCPD-isomers. This might effect the residence time though the error introduced is estimated not to exceed 10%. In view of the wide temperature range investigated, its effect on the values of the activation parameters can be neglected.

III-3 Discussion

The observed isomerisation of 1.5.5.-TMCPD to 1.2.3.-TMCPD and of 2.5.5.-TMCPD to 1.2.3.-TMCPD and to 1.2.4.-TMCPD clearly involves the formal shift of a methyl group from the geminally substituted allylic C_5-position to the adjacent carbon atoms C_1 and C_4.
If we exclude a polar mechanism for a reaction of a hydrocarbon in the gasphase two possibilities remain:
A) a free radical mechanism or:
B) an intramolecular multi-centre reaction.

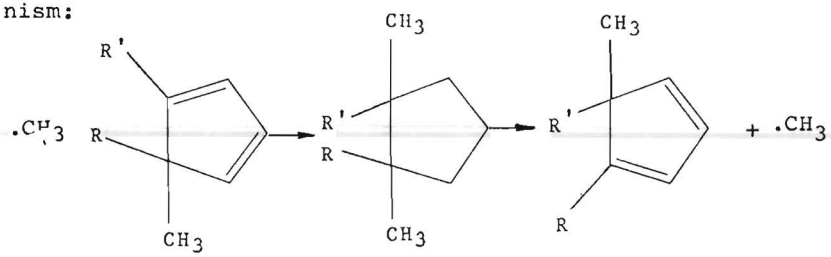
As to the former there are two possibilities:
a) a free radical dissociation -recombination reaction.
b) a free radical chain reaction.

a) The resonance energy of the cyclopentadienyl radical is not known. The observed energies of activation might however well be in accordance with a dissociation:



followed by a recombination. We reject this possibility for the following reasons. The two radicals do not move very far from each other before recombining since then an influence of inhibitors (trapping of methyl radicals)would occur. A cage-effect in the gas phase seems very unlikely. More convincing evidence is the exclusive formation of 1.2.3.-TMCPD from 1.5.5.-TMCPD and not of 1.2.4.-TMCPD. It is difficult to understand why recombination of a methyl radical with a 1.2-dimethyl-cyclopentadienyl radical does not give 1.2.4.-TMCPD as well.

b) The exclusive shift of a methyl group to an adjacent position can be explained by a free radical chain mechanism:



Experimental evidence against this mechanism is four-fold:
I) During the isomerisation reactions cyclopentadiene derivatives with abstractable hydrogen atoms are formed. One would expect these to react with any methyl radical present to yield a relatively stable cyclopentadienylic radical, thus terminating a chain reaction. The observed first order kinetics show the absence of an inhibiting effect of the products.
II) Similarly, propene, which is also known to act as a radical scavenger had no effect. (see figs. III-7 and III-8).

III) 2.5.5.-TMCPD rearranges about five times as fast as 1.5.5.-TMCPD in the temperature region investigated. If a radical chain reaction was involved, the methyl radicals split off by 2.5.5.-TMCPD might be expected to react with 1.5.5.-TMCPD. It was found, however, that addition of 15 mole % 2.5.5.-TMCPD to 1.5.5.-TMCPD does not influence the rate of isomerisation of the latter.

IV) Addition of di-tert.butyl-peroxyde to 1.5.5.-TMCPD and 2.5.5.-TMCPD has no influence on the rates of isomerisation as is evident from figs. III-7 and III-8. Di-tert. butyl-peroxyde decomposes according to the equation:

$$(CH_3)_3COOC(CH_3)_3 \longrightarrow 2\ CH_3COCH_3 + 2\ .\ CH_3$$

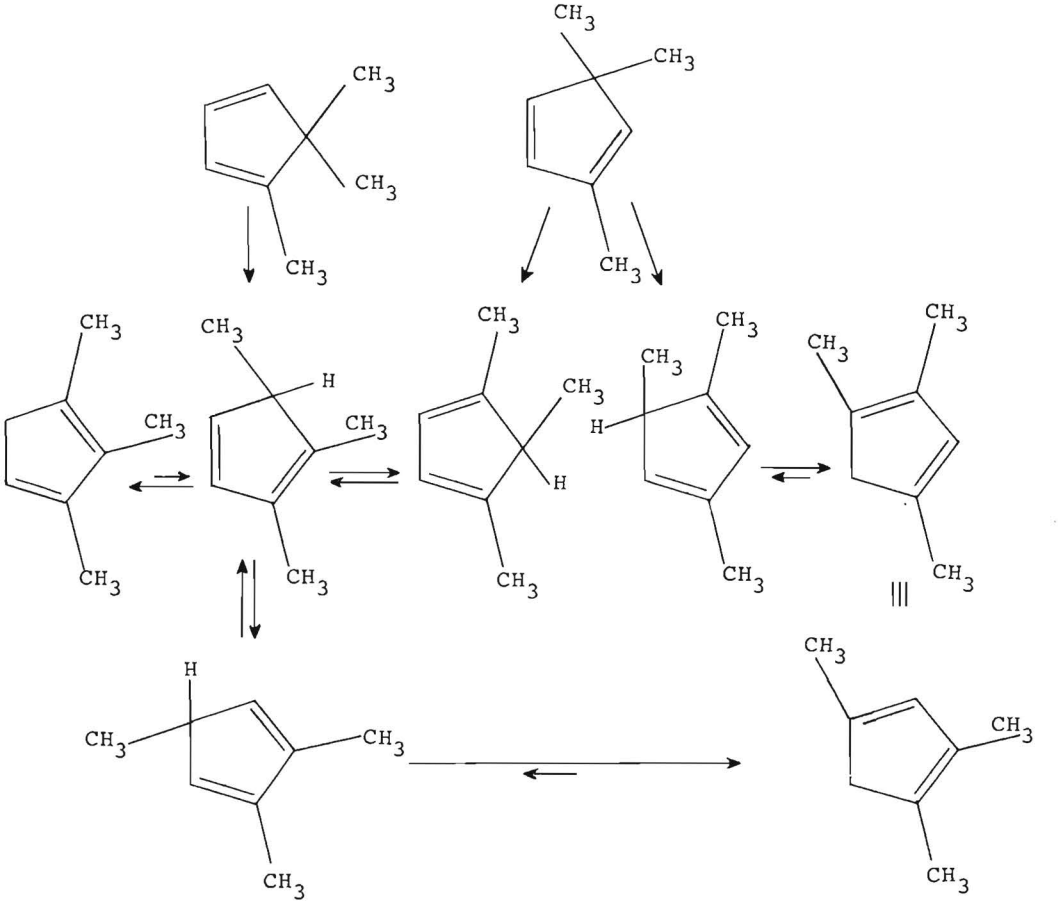
The rate of decomposition is given by:

$$k = 7.10^{15} \exp(-38000/RT)$$

which means that under the conditions of the isomerisations extensive formation of methyl radicals occurs. Since the rates of isomerisation are not influenced, it is assum-

ed that the methyl radicals do not initiate a radical chain reaction of the supposed type.

If polar and free-radical mechanisms are thus eliminated, it is concluded, that the observed skeletal isomerisations of geminal TMCPD isomers involve an intramolecular thermal 5 → 1 shift of a methyl group. The rearrangements are summarised by the scheme:



Vertical arrows indicate a 5 ⟶ 1 methyl shift.
Horizontal arrows indicate a 5 ⟶ 1 hydrogen shift.

The 5 ⟶ 1 shift of a methyl group is analogous to the 5 ⟶ 1 thermal hydrogen shift which has been investigated intensively by several investigators during the last few years. A number of those isomerisations were observed by

RIEMSCHNEIDER et al (refs 27,28,29) who did not give an interpretation of the results. MIRONOV et al (ref 23) devoted a comprehensive study especially to the class of the mono- and vicinally multi-methyl-substituted cyclopentadienes.The intramolecular character of the reactions was shown by denterium labelled C.P.D.:mass-spectrometry showed that no intermolecular redistribution of protons and deuterium atoms occured.Similar results were independently obtained by ROTH et al (ref 24) who prepared 5-H-perdeutero-C.P.D.

The sequence:

5-isomer ⟶ 1-isomer ⟶ 2-isomer

was established by NMR spectroscopy. For the reaction:

5-H-perdeutero-CPD⟶1-H-perdeutero-CPD

an energy of activation of 24.3 kcal/mole was obtained.The kinetics of the 5⟶1-H-shifts were further studied by McLEAN and HAYNES,again by means of NMR. For the reaction:

5-Me-CPD ⟶ 1-Me-CPD

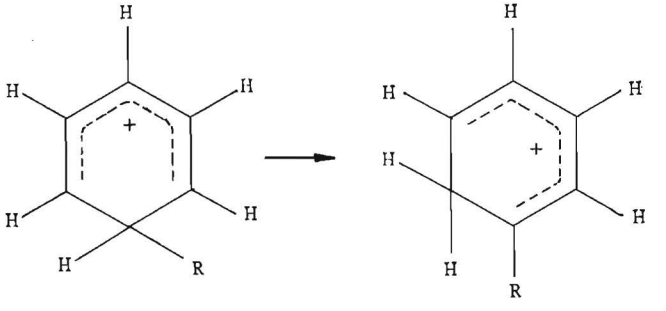
an energy of activation of 20.4 kcal/mole and an entropy of activation of -10 cal/degr.mole were found.It was shown further, that the reaction:

1-Me-CPD ⟶ 2-Me-CPD

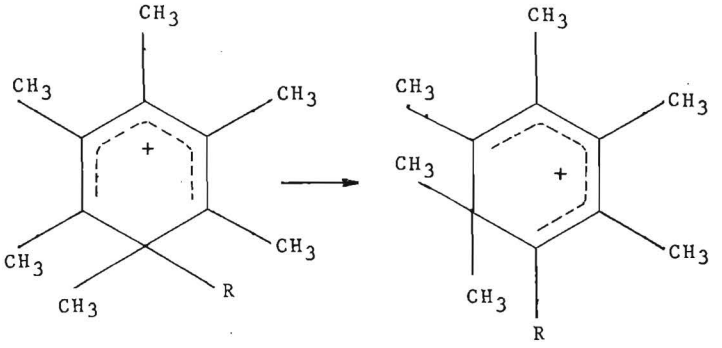
proceeds more slowly than the firstmentioned one.(ref30).

The just documented analogy in cyclopentadienes of the thermal intramolecular shift of a methyl group (described in this chapter) and the mentioned shift of hydrogen exists in two other systems: in benzenonium ions and, photochemically, in cycloheptatrienes:

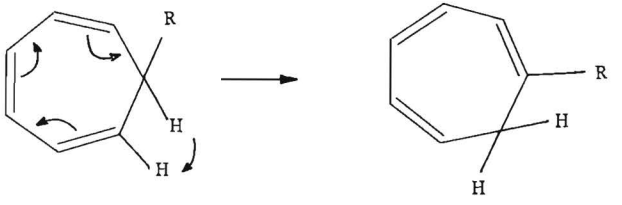
MACKOR and McLEAN (ref 31) observed a rapid (H = 8 kcal/mole) shift of hydrogen in hexa-methyl-benzene-proton complexes:



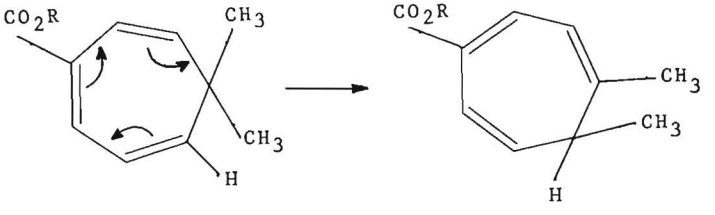
The corresponding methyl-shift has been found by DOERING and SAUNDERS (ref 32) in hepta-methyl-benzenonium ions:



In cycloheptatriene a photochemical intramolecular 7⟶1 shift of a hydrogen atom has been found by several investigators. (refs 33,34).



The analogous photochemical shift of a methyl group has been reported by CHAPMAN and SMITH (ref 35). Irradiation of methyl thujate yielded as the major product an isomer in which one of the methyl groups had shifted to an adjacent position.



Summarising, there exist three systems with analogous shifts of a hydrogen atom and a methyl group:

A thermal 1 ⟶ 5 shift in cyclopentadienes
A thermal 1 ⟶ 6 shift in benzenonium ions
A photochemical 1 ⟶ 7 shift in cycloheptatrienes.

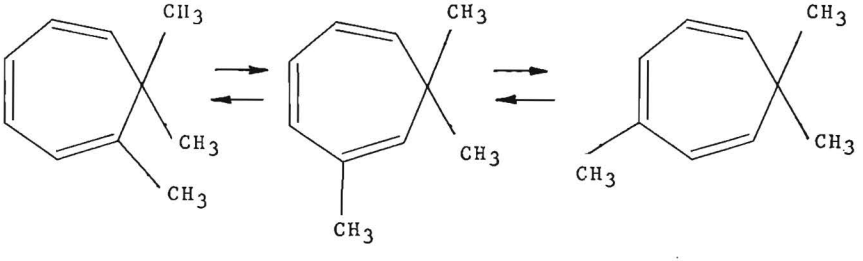
Since shifts of hydrogen are known in a number of other systems, the question arises whether the analogous shifts of methyl groups may also occur. Before going into this question, the very recent hypotheses of WOODWARD and HOFFMANN on "sigmatropic rearrangements" are recalled. They pointed out that the course of such isomerisations is determined largely by symmetry-relationships of the highest occupied orbitals. (ref 36).
In hydrogen migration within an all-cis poly-olefin framework with n conjugated double bonds the transition state was represented as the combination of one hydrogen atom and a radical containing (2n + 1) π-electrons. There are two possible ways of migration: in the first, called "suprafacial", the moving hydrogen is at all times associated with the same face of the π-electron system,the transition state thus possesses a plane of symmetry. In the second way,"antarafacial", the moving hydrogen passes from the top of one carbon terminal to the bottom of the other, the transition state than possesses a two fold axis of symmetry.
For the symmetry of the highest occupied ground-state orbital in the framework system it was concluded that, in order that positive overlap between the framework orbital and the hydrogen orbital be maintained, the isomerisation takes place thermally by the suprafacial route when n is even and by the antarafacial route when n is odd. When a system is photochemically brought into an excited level,

the symmetry of the highest occupied orbital changes and the selection rules just reverse.
In small or medium-sized rings only suprafacial shifts are possible. These may occur thermally 1 ⟶ 5 or photochemically 1 ⟶ 3 and 1 ⟶ 7. All these kinds of shifts have been reported for hydrogen.Analogous methyl shifts,however,

have so far only been reported between adjacent carbon atoms in ring systems.
The hydrogen 1-s orbital, involved in σ-bonding with the ring carbon atoms, is spherically symmetrical. Therefore hydrogen migrations will not be very sensitive to stereochemical conditions. If a methyl group migrates in a tetrahedral state, one of its sp^3 orbitals is involved in the interaction with the frame of the carbon atoms. Evidently full benefit of overlap will be achieved if both ends of the carbon chain are located underneath the inverted umbrella.

If a methyl group in the transition state is trigonal, than a p-orbital is involved. The symmetry of the latter is such that the selection rules just reverse.

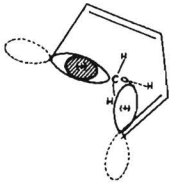
Relatively rapid transannular 1 ⟶ 5 shifts of hydrogen have been shown to occur thermally in cycloheptatriene and dihydrotropone. The thermal behaviour of the properly substituted trimethyl-derivatives have been investigated by BERSON and WILLCOTT (ref 37): at 300°C the three possible geminal TMCHT's are in thermal equilibrum:



The mechanism was revealed by D-labelling as a true skeletal reorganisation of ring carbons rather than a consecutive series of methyl shifts.
In e.g. the case of cycloheptatriene two transition states can be visualised. If the migrating methyl group is trigonal, than the 1 ⟶ 5 shift is forbidden by the selection rules. In the case of a tetragonal transition state the shift of the non spherically symmetrical, sterically hindered methyl group would require considerable reorientat-

ion. This reorientation might be prohibitive for the reaction to occur:

1 ⟶ 5 and 1 ⟶ 7 shifts of hydrogen are known in 1,3 dienes and in 1,3,5-trienes. It might well be that corresponding methyl shifts are less likely because the approach of the receiving carbon atom is sterically hindered.



The enumarated three shifts of hydrogen that have a methyl migrating counterpart the situation as depicted in the figure is ideal. In each of the systems the donating and receiving carbon atoms are close together since in the initial and in the final state they are connected by a single bond. In the transition state they are thus also favourably located underneath the methyl group.

CHAPTER IV

STRUCTURE ASSIGNMENTS AND SPECTRA OF THE TRI-METHYLCYCLOPENTADIENE (TMCPD) COMPOUNDS

IV-1 General

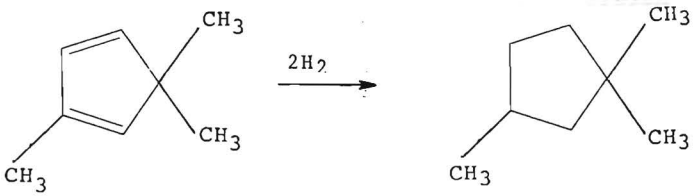
In chapter III it was shown that thermolysis of bornyl- and isobornyl acetate yields four major products. The determination of the structures of these products proceeds in three distinct steps:

a) Determination of the molecular formula.
b) Determination of the overall molecular skeleton.
c) Assignment of isomeric structures.

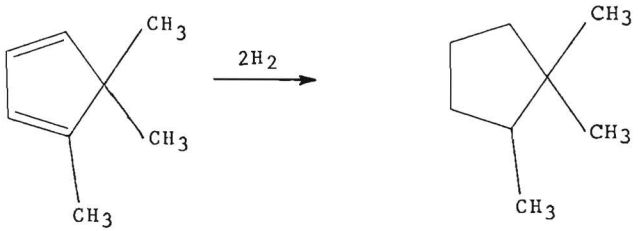
These four compounds are formed by thermolysis of bornyl- and isobornyl acetate, so only carbon, hydrogen and oxygen are possibly present. Their IR spectra showed no absorptions in the regions, characteristic of -COH, C-O and C=O bonds. Hence they are hydrocarbons. The mass spectra revealed a molecular weight of 108 for each of the compounds indicating a molecular formula C_8H_{12}. Thus they contain three double bonds and/or rings. All of them absorb in the 240-260 nm region of the UV spectrum with extinction coefficients of the order of 10^4, characteristic of two conjugated double bonds (ref. 38). Thereby bicyclic and tricyclic structures are ruled out. On hydrogenation each of them takes up two equivalents of hydrogen to give trimethyl-cyclopentanes (TMCP's). In the IR and NMR spectra no indications are found for the presence of exo-methylene groups. This suggests, that we are dealing with four isomeric tri-methyl-cyclopentadienes (TMCPD's).

Finally the positions of the three methyl groups with respect to the double bonds remain to be established for each of the isomers separately. For convenience the two low-boiling TMCPD's (see chapter III) will be discussed separately from the high-boiling TMCPD's, i.e. the two compounds, obtained by thermal rearrangement of the two first-mentioned isomers. In the following they will be referred to as A,B and E, F respectively.

The two low-boiling TMCPD's, A and B, yield 1.1.3.-TMCP and 1.1.2.-TMCP respectively on hydrogenation. Since there was sufficient evidence, that isomerisation has not taken place, this is only consistent with the structures 2.5.5.-TMCPD and 1.1.5.-TMCPD respectively:



and



These structures are also confirmed by UV- and IR-spectroscopy. (see IV-3, discussion of the spectra). In the NMR-spectra the different types of protons are easily distinguished by their chemical shifts. For compound A NMR signals occur at τ= 3.7, τ= 3.9, τ= 4.2, τ = 8.1 and τ = 8.8[5] with relative areas of 1:1:1:3:6. For compound B the data are τ= 3.8, τ = 4.1, τ = 8.2 and τ = 8.9[5] with relative areas of 2:1:3:6. The signals between τ= 3.7 and τ = 4.2 belong to olefinic protons and the signals near τ =8.2 and τ = 8.9 to methyl groups, attached to the olefinic carbons and to the allylic C_5-position respectively. The integrated spectra establish firmly the exclusive presence of three olefinic protons, one "olefinic" methyl group and an allylic geminal di-methyl group (at C_5). The determination by NMR of the position of the "olefinic" methyl group requires a more detailed study of the spectra of A and B (see IV-3-4).

E, the low boiling isomer of the two "secondary" TMCPD's yields on hydrogenation a mixture of 1-cis 2-trans 4-TMCP and 1-trans 2-cis 4-TMCP, while F yields a mixture of all three isomeric 1.2.3.-TMCP's. The positions of the methyl groups relative to each other are thus established.
The positions of the double bonds with respect to the methyl groups are unambiguously proved by NMR spectroscopy. In the spectra of E and F signals are found at τ = 4.1, τ = 7.3 and τ =8.0-8.2 with relative areas of 1:2:9.No signals are found in the region, characteristic of methyl groups, attached to the allylic C_5-position (τ =8.9, see before). Thus only one olefinic proton per molecule is found (τ = 4.1). The signals near τ = 7.3 are ascribed to the two allylic protons. In combination with the hydrogenation results each of the above mentioned three arguments, abstracted from the NMR spectra is already sufficient to establish the structure.

Based on the above mentioned data the 1.2.4.-TMCPD structure is assigned to compound E and the 1.2.3.-TMCPD structure to compound F. This is substantiated further by a detailed study by means of double resonance of the allylic spin multiplet patterns (see IV-3-4). The structures are also confirmed by IR- and UV spectroscopy.

IV-2 Experimental

IV-2-1 Hydrogenation

Tri-methyl-cyclopentadienes were converted to the corresponding tri-methyl-cyclopentanes by absorption of two moles of hydrogen according to the equation:

$$C_8H_{12} + 2H_2 \xrightarrow{\text{cat}} C_8H_{16}$$

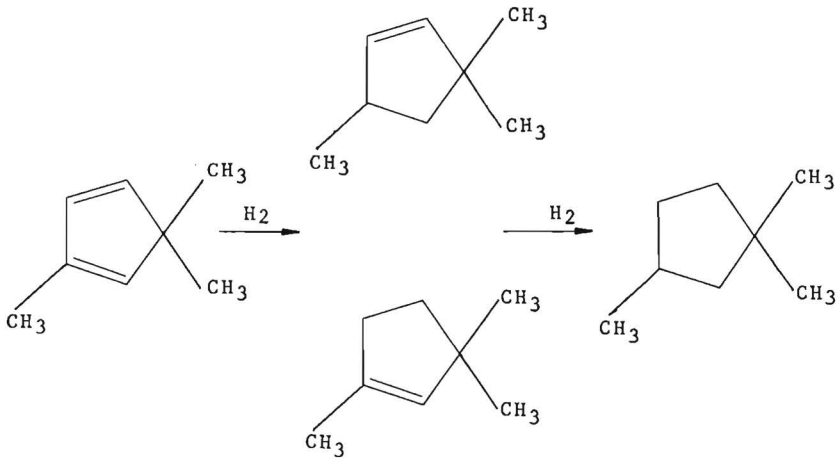
The resulting cyclopentane derivatives were compared with API samples of known structures.

It should be borne in mind, that application of hydrogenation in the process of elucidating structures is confined to those cases, where skeletal isomerisations of the reactants do not occur. Treating the four TMCPD's with the catalyst under the reaction conditions but with exclusion of hydrogen was found to have no effect. I ml samples of

the TMCPD's were hydrogenated at atmospheric pressure over a palladium catalyst. The reaction vessels were heated with an infrared lamp to about 60°C. The absorbed quantities of hydrogen were measured with the aid of a calibrated vertical glass cylinder, filled with water. The results of the hydrogenation experiments will now be given for each of the TMCPD's separately. The methods of analysis will be discussed at the end of this sub-section.

Compound A

This compound was not readily hydrogenated. The process proceeded stepwise as was proved by GLC and by mass spectroscopy (MS). Two C_8H_{14} intermediates were observed.After 8 hrs a mixture was formed which contained over 50% of 1.1.3.-TMCP, indentified by its retention time on a squalane column and by its NMR-spectrum.



Compound B

One equivalent of hydrogen was absorbed within half an hour. After 2 hrs a mixture was formed, containing about 65% of a compound with rrtS = 1.85 and approximately 35% of a compound with rrtS = 1.56. The main compound was identical to 1.1.2.-TMCP. The minor compound had the molecular formula C_8H_{14} according to its mass spectrum. Extra NMR signals at τ = 8.35 (doublet, J = 1.7 cps) indicated

that the C_8H_{14} intermediate is most probably 1.5.5.-trimethyl-cyclopentene.

Compound E

No intermediates were observed in this case. After 2 hrs the hydrogenation was completed. MS analysis showed, that the reaction product mixture consisted exclusively of C_8H_{16} isomers. GLC analysis indicated that 60% of the mixture consisted of 1-trans 2-cis 4-TMCP and 40% of 1-cis 2-trans 4-TMCP. These results were substantiated by NMR spectroscopy, since all characteristic methyl resonances at τ-values of 8.92, 8.96, 9.04, 9.11 and 9.20 were found.

Compound F

At the time that the hydrogenation experiments were performed, F was only available in a 60-40% mixture with compound E. After 5½ hrs of hydrogenation a mixture was formed, containing five C_8H_{16} isomers. Apart from 1- trans 2-cis 4-TMCP and 1-cis 2-trans-4-TMCP (about 56% together) all three possible 1.2.3.-TMCP's were detected by GLC.This was also consistent with the NMR spectrum. The hydrogenation of compound F proceeded via 1.2.3.-tri-methyl-cyclopentene as was found by GLC comparison with a product which was prepared by heating F at 320°C in a glass ampoule (see III-3).

Identification of the hydrogenation products

All hydrogenation products were easily identified by GLC comparison with API standard samples. A 4 m squalane column at 80°C was used, in a few cases also a 4 m Apiezon-L column at 80°C was applied. In table IV-I the retention times of all pertinent compounds are given relative to that of compound A, the lowest boiling compound of the series. The retention times of the corresponding cis/trans 1.2.3.- and 1.2.4.-TMCP's turned out to be very similar. The differences were, however, large enough to justify a distinction between the 1.2.3.- and 1,2,4,-configurations of the TMCPD's.

Table IV-I Retention times of TMCPD's and TMCP's relative to 2.5.5.-TMCPD on a 4m squalane column at 80°C.

Compound	rrts
A (2.5.5.-TMCPD)	1.00
A'	1.31
B (1.5.5.-TMCPD)	1.17
B'	1.41
E (1.2.4.-TMCPD)	2.76
F (1.2.3.-TMCPD)	3.29
1.1.3.-TMCP	1.37
1.1.2.-TMCP	1.86
1.t2.c4.-TMCP	1.52
1.c2.t4.-TMCP	1.99
1.c2.t3.-TMCP	2.04
1.t2.c3.-TMCP	1.59
1.c2.c3.-TMCP	2.52

A' and B' refer to compounds, formed by rearrangement during the purification of A and B by preparative gaschromatography (see chapter III). The structures will be discussed in IV-3. As a second means of distinction NMR spectroscopy was applied. The spectra were not analysed completely. Only the methyl signals were used for comparison in a fingerprint fashion. The results are summarised in table IV-2.

Table IV-2 Methyl resonances in the 40 Mc NMR spectra of TMCP isomers (in cps downfield from TMS).

Compound	Methyl resonances			
1.1.3.-TMCP	41.6	39.2	36.8	
1.1.2.-TMCP	38.4	30.4		
1-t2-c4-TMCP	41.6	35.6		
1-c2-t4-TMCP	43.2	38.4	32.0	
1-c2-t3-TMCP				
1-t2-c3-TMCP	40.8	36.8		
1-c2-c3-TMCP	40.0	34.4	28.8	22.4

IV-2-2 UV spectra

All ultraviolet spectra were measured in cyclohexane solutions on a Cary 14 instrument.

IV-2-3 IR spectra

All infrared spectra were measured on a Perkin Elmer 237 instrument. Carbon tetrachloride was used as a solvent in the 4000-900 cm^{-1} region and carbon disulfide in the 900-650 cm^{-1} region. The oncentrations were about 10% w/w.

IV-2-4 NMR spectra

The NMR spectra were run on a Perkin Elmer 40 Mc instrument in carbon tetrachloride solutions with tetramethylsilane as an internal reference.

IV-3 Discussion

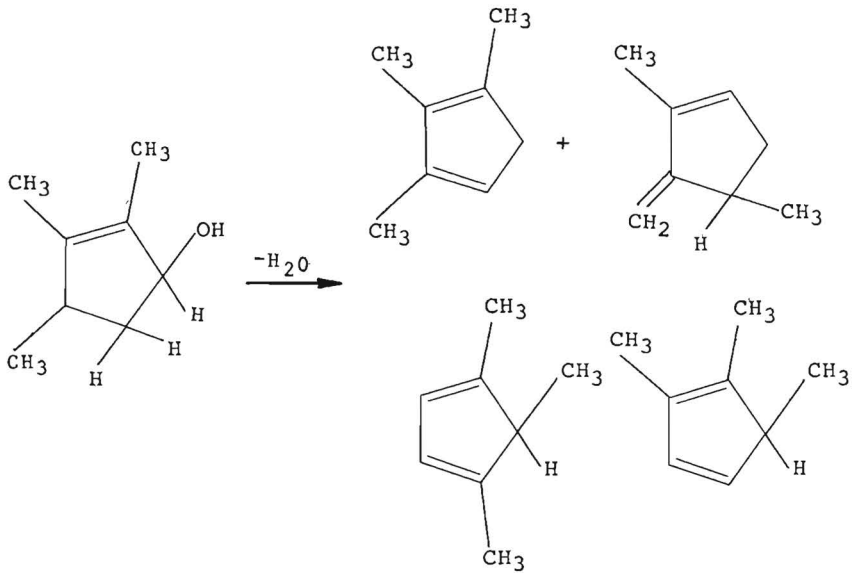
IV-3-1 Literature data

It was shown in chapter III that in cyclopentadienes relatively fast thermal 5⟶1 shifts of hydrogen occur which cause rapid interconversions of a number of TMCPD isomers. The early work of DAMSKY (ref 26) who was the first to prepare a tri-methyl-cyclopentadiene by dry distillation of a mixture of calcium camphylate and sodium oxyde, has already been mentioned in III-1. ALDER and MUDERS (ref 39) recently reinvestigated Damsky's method of preparation. Diene synthesis with ethylene resulted in the formation of ξ-fenchene as shown by IR spectrometry. They found that hydrogenation yielded 1.2.3.-tri-methyl-cyclopentene as an intermediate. ALDER and MUDERS concluded therefore, that Damsky's hydrocarbon was 1.2.3.-TMCPD.Most probably Damsky's hydrocarbon also contained some H-shift isomers: 1.2.5.-TMCPD and 1.4.5.-TMCPD (see before).

ALDER and MUDERS , when carrying out the reaction under less drastic conditions, obtained a hydrocarbon the structure of which was different from the previous one and was

found to be 1.5.5.-TMCPD. On the base of present day knowledge it contained probably some 1.2.3.-TMCPD as well. (see III-2-2).

A series of vicinal tri-substituted CPD's were prepared by MIRONOV c.s. (ref 23) by dehydration of 1.2.3.-tri-methyl cyclopentane-5-ol:



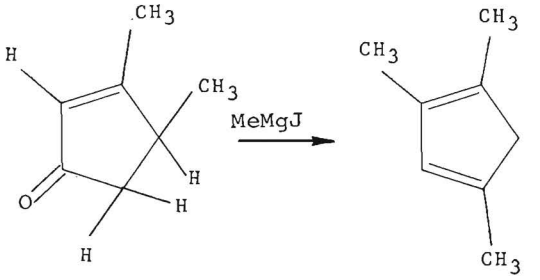
The structures were confirmed by adduct formations and by IR spectrometry. 1.2.3.-TMCPD and its exocyclic double bond derivative were found in a 7:3 ratio approximately. A mixture of 1.2.5.-TMCPD and 1.4.5.-TMCPD was prepared by careful distillation of the equilibrium mixture, which contained about 95% of the 1.2.3.-isomer.

MIRONOV was the first to account for the rapid 5⟶1 H-shifts.

AUTERINEN (ref 40) prepared 2.5.5.-TMCPD in the following way: 1.3.3.-tri-methyl-cyclopentene yielded on bromination a dibromine adduct. Dehydrobromation in boiling quinoline at 235°C resulted in the formation of 2.5.5.-TMCPD. The relative positions of the methyl groups were established by catalytic hydrogenation to 1.1.3.-tri-methyl-cyclopen-

tane (identified by IR spectrometry). Most probably,however, AUTERINEN's product was contaminated with 1.2.4.-TMCPD, 1.2.3.-TMCPD and their possible H-shift isomers since it was shown in III-3, that 2.5.5.-TMCPD isomerises even more readily than 1.5.5.-TMCPD.

NAZAROV and ELIZAROVA (ref 41) prepared 1.2.4.-TMCPD:



Since only hydrogenation to 1.2.4.-TMCPD was mentioned as a means of structure confirmation, we assume, that again H-shift isomerisation must have caused the presence of some 1.3.5.- and 2.3.5.-TMCPD as well.

IV-3-2 UV spectra

CSICSERY investigated the ultraviolet spectra of the three mono-methyl-cyclopentadienes (ref 42). Cyclopentadiene itself is known to have its maximum absorption at 240 nm. CSICSERY found, that mono-methyl substitution at the C_5 position causes a hypsochromic shift of about 2 nm whereas methyl substitution at the 1- and 2-positions causes batochromic effects of 9 nm and 3 nm respectively. Assuming that the effects of more methyl groups are additive, the values of λ_{max} for the various TMCPD's were calculated.The results are compared with the experimental values for λ_{max} in Table IV-3.

It is seen, that the agreement between calculated and experimental values for the two geminally substituted isomers is very good. Of the three H-shift isomers 1.2.4.-TMCPD, 1.3.5.-TMCPD and 2.3.5.-TMCPD only the first has a calculated maximum which is in good agreement with the experimental value. Of the other set of three H-shift iso-

mers only the 1.2.5.-configuration can be ruled out by the above data.

Table IV-3 Calculated and experimental values for the ultraviolet absorption maxima of TMCPD isomers.

Isomer	Calculated	Experimental
2.5.5.-TMCPD	240-2x2+3=239 nm	239 nm(compound A)
1.5.5.-TMCPD	240-2x2+9=245 nm	244 nm(compound B)
1.2.4.-TMCPD	240+2x9+3=262 nm	260 nm(compound E)
1.3.5.-TMCPD	240-2+3+9=250 nm	---
2.3.5.-TMCPD	240-2+3+3=244 nm	---
1.2.3.-TMCPD	240+2x3+9=255 nm	254 nm(compound F)
1.2.5.-TMCPD	240-2+3+9=250 nm	---
1.4.5.-TMCPD	240-2+9+9=256 nm	---

IV-3-3 IR spectra

IR spectroscopy constitutes a very suitable means for making a distinction between the two pairs: A,B and E,F. The spectra provide less means for a distinction between A and B or between E and F. The C-H stretchings for tri-and cis-disubstituted ethylenes are usually found between 3045cm^{-1} and 3015cm^{-1} with medium intensities (ref43a).In the spectra of A and B relatively strong absorptions are found in this region, indicating the presence of at least one C=C-H bond per molecule. No indications are found for the presence of exocyclic $=CH_2$ groups. The CH_3-stretchings absorb normally near 2962 cm^{-1} and 2872 cm^{-1} (ref 43b).Unfortunately the main frequencies are not altered very much when the methyl groups are attached to different environments. In all four spectra strong absorptions are found in this region indicating the presence of methyl groups. The doublet absorptions, characteristic of geminal methyl groups (ref 43 b) are found at 1379-1353 cm^{-1}for A and at 1378-1354 cm^{-1} for B. The low frequency part had a larger amplitude, pointing to the possible presence of a third methyl group.

Normally n conjugated double bonds give rise to n absorption bands in the C=C stretching region of the IR spectrum. The intensities are enhanced compared with non-conjugated double bonds. In most cases the strongest band appears near 1650 cm^{-1} (ref 43c). Furthermore it is known, that the frequency falls with increasing ring strain. In cyclobutene e.g. the frequency is at 1566 cm^{-1}, while 1568 cm^{-1} is found for the highly strained bicyclo-heptenes (ref 43d). In the cyclopentadiene ring the strain is perhaps comparable with that of cyclobutene. Methyl substitution lowers the effect of ring strain as has been shown for bicyclo-heptenes (ref 43d). A similar effect might be expected for the substitution of the cyclopentadiene ring. Moreover the frequency will rise with increasing double bond substitution since tri- and tetra substituted double bonds absorb usually at higher frequencies than cis-disubstituted double bonds.

The two effects will most probably be summed in the spectra of the tri-methyl-cyclopentadienes. In cyclopentadiene itself two bands are observed at 1590cm^{-1} and at 1610cm^{-1}. In the mono methyl derivatives 1620 cm^{-1} was found for the 2-isomer and 1610 cm^{-1} for the 1-isomer. The strongest bands in A and B are at 1622 cm^{-1} and at 1613 cm^{-1} respectively. These values are compatible with the proposed structures. In the spectra of E and F relatively weak absorptions are found in the C=C-H stretching region near 3050 cm^{-1}, corresponding with the presence of one such group. Apart from the absorptions, due to methyl stretchings near 2960 cm^{-1} and 2870 cm^{-1}, also bands are found near 2930 cm^{-1} and near 2850 cm^{-1}. These are ascribed to methylene groups. In the C=C stretching region near 1650 cm^{-1}, E and F absorb at 1645 cm^{-1} and at 1648 cm^{-1} respectively. These values are considerably higher than those for A and B. This is consistent with a high degree of substitution of the double bonds (see before).

IV-3-4 NMR spectra

The same difficulties as with the IR spectra are encountered: the distinction between the pairs A,B and E,F is very simple by a comparison of the overall spectrum app-

earance whereas the distinction in each pair becomes much more intricate. In principle the means of distinction are provided by relatively small differences in chemical shifts and spin multiplet patterns when a methyl group and a proton are interchanged.

Chemical shifts

The allylic methyl groups in the spectrum of compound B are found at 0.11 ppm to higher fields as compared with compound A. A similar difference is found for the third methyl group: 0.08 ppm. The proton at C_1 in 2.5.5.-TMCPD is found at a higher field (0.08 ppm) than the corresponding proton at C_2 in 1.5.5.-TMCPD.
The relative positions of the methyl groups in the 1.5.5.-isomer should result in larger mutual shielding effects and hence to higher τ-values for the appropriate signals as in the 2.5.5.-configuration. This is illustrated in fig.IV-1. Of course shielding by other neighbouring groups and bond has also an effect upon the methyl chemical shifts.

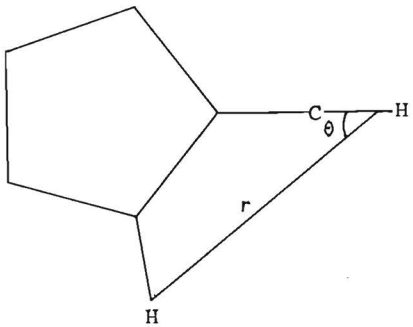


fig IV-1

The shielding of a particular proton by a neighbouring anisotropic bond is given by McConnell's formula:

$$\sigma_{av} = \frac{(3\cos^2\theta - 1)\ (\chi_{//} - \chi_{\perp})}{3r^3}$$

r stands for the distance between the centre of gravity of the anisotropic electron cloud and the screened proton(s) and θ is the acute angle between the symmetry axis of the electron cloud and the direction of r. $\Delta\chi$ is the magnetic bond anisotropy. For C-H, C-C and C=C bonds the $\Delta\chi$ -values

are all negative: -3.10^{-30}, -5.10^{-30} and -10.10^{-30} cm^{-3} respectively (ref 44). Therefore negative σ_{av} - values are found for $\theta < 55^{o}44'$. Now a semi-quantitative estimate will be made for the effects in 1.5.5.-TMCPD and 2.5.5.-TMCPD. For convenience a model is taken in which all bond lenghts and angles are equal. The effect of a methyl group is simulated by taking the centre of gravity at 1.30 A from the ring carbon while the total bond anisotropy is taken twice as large as that of a C-C bond.

If a methyl group or a proton is displaced from the 1- to the 2-position, the shielding by the C_5-C_1=C_2-C_3 part of the ring remains the same, assuming that the bonds C_5-C_1 and C_2-C_3 are equal. The mutual shielding between the interchanged methyl groups and proton remains also constant. Therefore the only variables are the shielding by the C_3=C_4, C_4-C_5, and C_3-H bonds and by the geminal methyl group. These effects were calculated for the C_1 proton in 2.5.5.-TMCPD and the C_2 proton in 1.5.5.-TMCPD.

2.5.5.-configuration

a) Shielding by geminal methyl group:	+ 0.26 ppm
b) Shielding by C_3 = C_4 bond:	+ 0.08 ppm
c) Deshielding by C_5-H bond:	- 0.26 ppm
d) Deshielding by C_3-H bond:	- 0.02 ppm
Total effect:	+ 0.06 ppm

1.5.5.-configuration

a) Shielding by geminal methyl group:	- 0.02 ppm
b) Deshielding by C_3 = C_4 bond:	- 0.52 ppm
c) Shielding by C_5-C_1 bond:	+ 0.04 ppm
d) Shielding by C_3-H bond:	+ 0.26 ppm
Total effect:	- 0.24 ppm

Hence, according to this equation, the proton at C_1 in 2.5.5.-TMCPD should be found at 0.30 ppm to higher fields than the corresponding proton at C_2 in 1.5.5.-TMCPD. The actual difference was 0.08 ppm. In a similar way it is calculated, that the methyl group at C_2 in 2.5.5.-TMCPD

should resonate at a lower field (0.56 ppm) than the methyl group at C_1 in 1.5.5.-TMCPD. Actually a difference of 0.08 ppm is found. In both cases the sign of the actually found difference is in accordance with the calculated effect. For the geminal methyl groups the only variables are the different shieldings, experienced from a methyl group or a proton in a 1- or a 2-position. Shieldings by groups in the latter position will virtually be zero. From the effect of the substituent in the 1-position an upfield shift of 0.11 ppm is calculated. The actual shift between the geminal methyl groups in 1.5.5.-TMCPD and 2.5.5.-TMCPD is 0.11 ppm, again with the correct sign.

Hyperfine structure

Now a discussion will be given of the detailed analysis of the spin multiplet patterns in the NMR spectra of compounds A and B and of compounds E and F to distinguish between the isomeric structures in each of the pairs. In most cases use was made of the spin decoupling or "double resonance" technique in the frequency sweep mode. The method has been described in detail by FREEMAN and ANDERSON (refs45,46). When applying frequency sweep, a constant main magnetic field and irradiation frequency can be used. In this manner the centre of irradiation can be left exactly in position during the scanning of the rest of the spectrum, in contrast to the magnetic field sweep mode. When $(\nu_1-\nu_2)<50$ Hz so-called wiggles appear from an interaction of the irradiating and the scanning frequencies. Hereby the centre of irradiation can be located in the spectrum by applying a low-intensity irradiation frequency and simultaneously scanning the spectrum by frequency sweep. The center of irradiation than coincides with the centre of the wiggle pattern, which is superposed on the spectrum. The centre of irradiation can be displaced between different runs by slight adjustments of the main magnetic field.

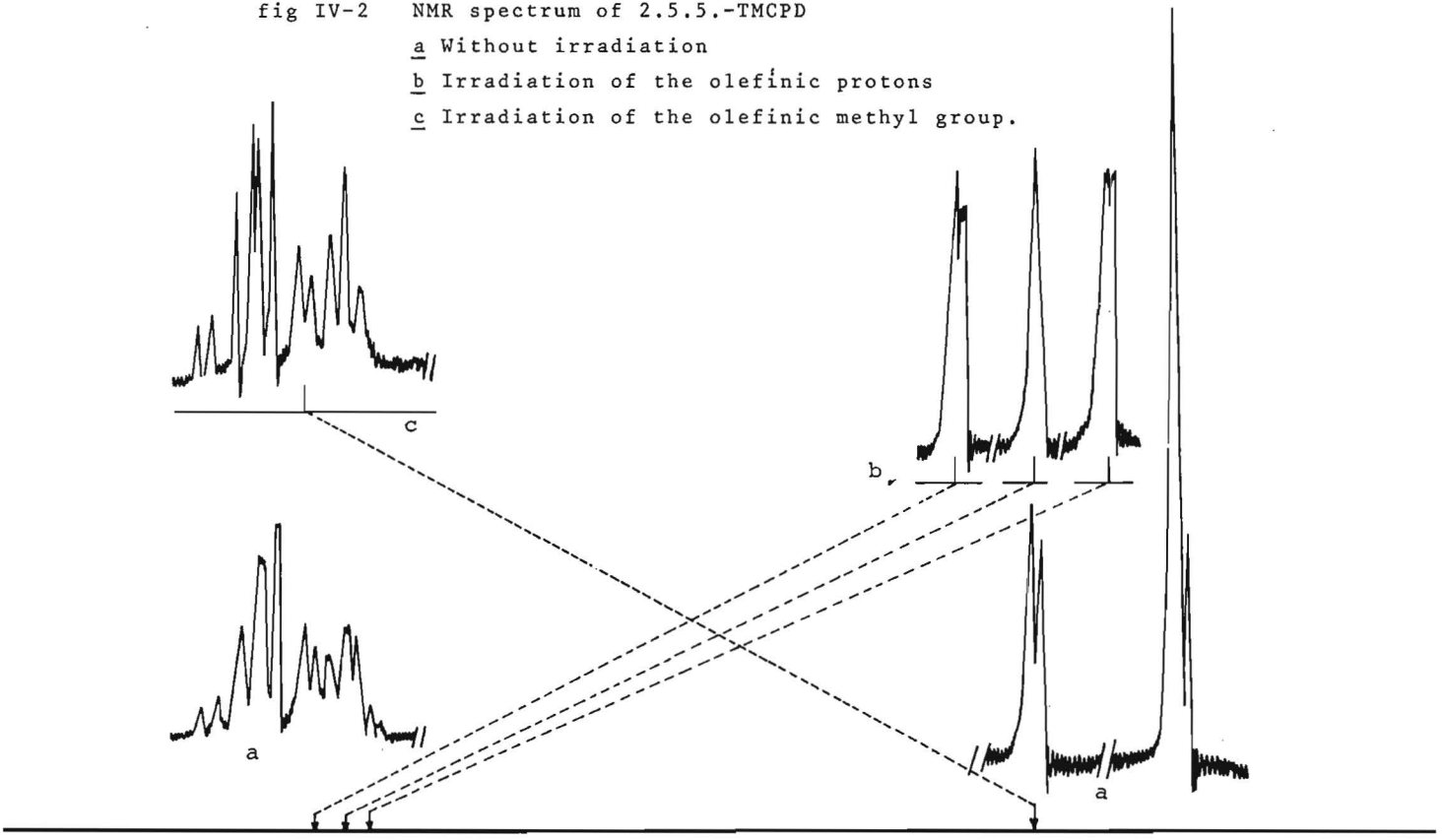
In the next example it will be shown how this technique can be used to find chemical shifts which cannot be evaluated in a direct way from the spectrum. Consider an AMX

fig IV-2 NMR spectrum of 2.5.5.-TMCPD

a Without irradiation

b Irradiation of the olefinic protons

c Irradiation of the olefinic methyl group.



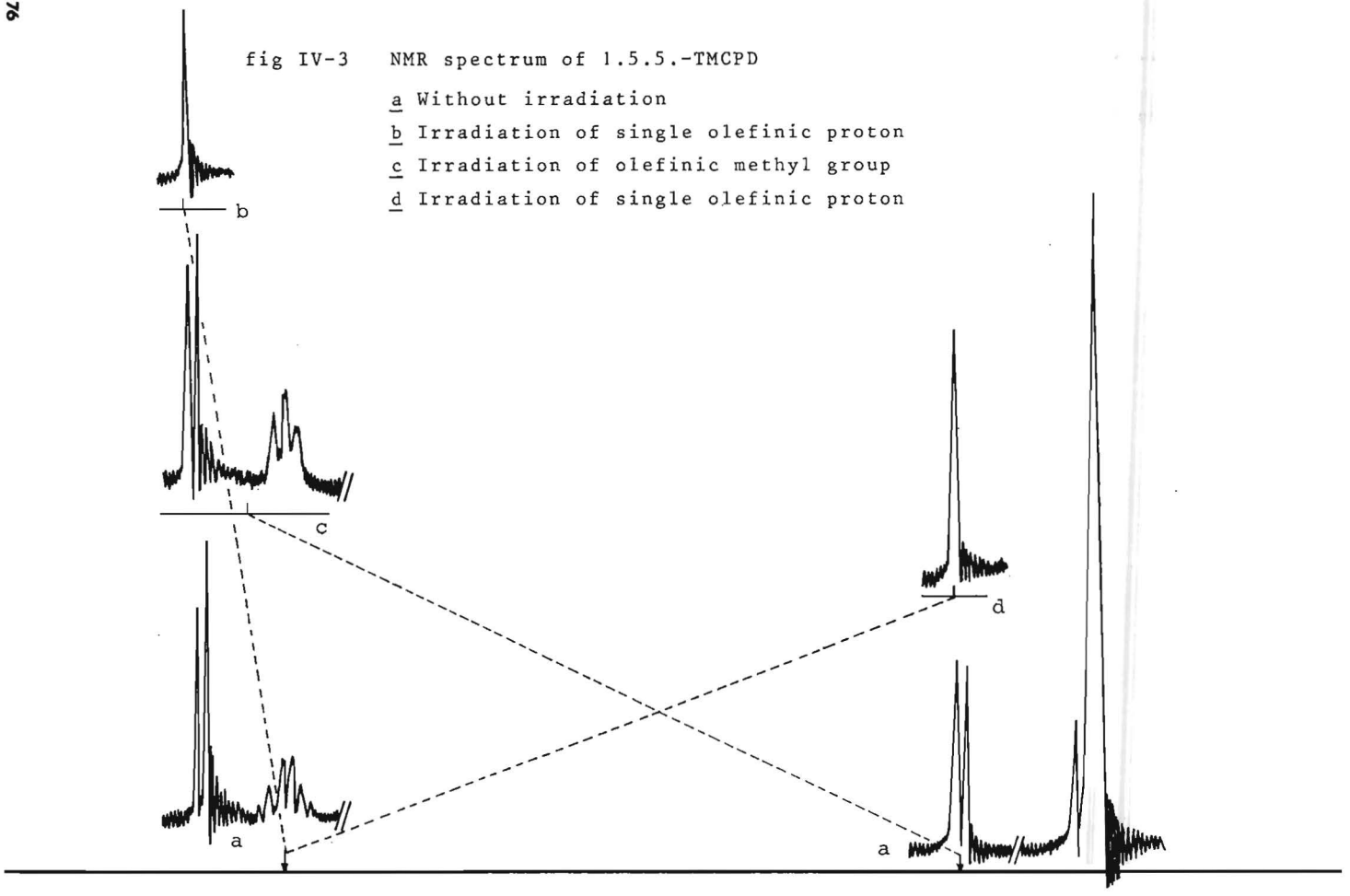


fig IV-3 NMR spectrum of 1.5.5.-TMCPD

a Without irradiation

b Irradiation of single olefinic proton

c Irradiation of olefinic methyl group

d Irradiation of single olefinic proton

system with J_{AM} = 1 cps, J_{AX} = 6 cps and J_{MX} = 0. The A-signal is easily recognised in the spectrum, Both M and X are coupled also to other protons in the molecule while moreover their signals overlap partially with those of the rest of the spectrum. Now an irradiation level is applied which is high enough to decouple A and M. A number of successive runs is made in which the A-signal is scanned for different positions of the irradiation frequency. The position for which the maximum decoupling with respect to J_{AM} is observed in the A-signal, corresponds with τ_M. After that the procedure is repeated with a higher irradiation level to find τ_X in the same way. According to the method outlined above, chemical shifts have been determinated in this study with an accuracy of ± 0.1 cps (± 0.025 ppm).

Firstly the spectra of compounds A and B will be discussed. The complete spectra are shown in figs. IV-2a and IV-3a respectively. At first sight the olefinic parts ($\tau \simeq 4$) look very different. It should, however, be borne in mind that in ABC systems with similar τ- and J-values relatively small differences may result in large effects on spectrum appearance.

In the spectrum of compound B two clearly separated parts show up in the olefinic region: a doublet at τ= 3.79 (J= 1.8 cps), representing two protons and a sextet (J= 1.8 cps) at τ = 4.10, representing one proton. The doublet structure at τ = 3.79 completely collapses by irradiation of the sextet at τ = 4.10. (see fig. IV-3b). Conversely, the sextet is reduced to a quadruplet by irradiation of the signal at τ = 3.79. This suggests firstly, that two of the olefinic protons have the same chemical shift and, secondly, that the lone proton at τ = 4.10 is coupled to the methyl group at C_1 and to the other two olefinic protons with equal coupling constants (real or "virtual" as a consequence of the very similar chemical shifts of the protons at C_3 and C_4). The lone proton pattern is a sextet with binomial intensity ratios as is to be expected from a combination of one quadruplet and two doublet splittings with equal spacings.

This was substantiated further by irradiation of the methyl group signal at τ = 8.10. A triplet at τ = 4.10 is

observed, whereas the signal at $\tau = 3.79$ is not affected. In the counterpart experiment the methyl doublet collapsed by irradiation of the sextet signal. The sextet has to be ascribed most probably to the proton at C_2 since this is closest to the methyl group. Couplings of this type are known to be in the order of 1.6 to 2.0 cps. Coupling with the proton at C_3 can, however not be ruled out without further evidence.

In the spectrum of compound A the olefinic part looks like an ABC system in which the C-part is spoiled by additional couplings. The AB-part seemes to be broadened as well. By a combination of spin decoupling and frequency sweep it was possible to determine the chemical shift of that proton, which is coupled to the olefinic methyl group with J= 1.7 cps (see fig. IV-2b). This proton was most probably H_1. A value of $\tau_1 = 4.18$ was found. The secondary broadening effect in the methyl doublet at $\tau = 8.10$ has to be ascribed to coupling with the two other olefinic protons. By irradiation of the methyl signal ($\tau = 8.10$) the ethylenic multiplet was reduced to an ABC spectrum with equal J_{AC} and J_{BC} (see fig. IV-2c). Unfortunately the τ-values could not be attributed to specific protons with the exception of the signal at $\tau = 4.18$ which was assigned to H_1. This signal correspondes to the C-part in the ABC system already mentioned. On irradiating the $\tau = 8.10$ methyl signal, the $\tau = 4.18$ olefinic signal appeares as a triplet with spacings of 1.7 cps, in agreement with $J_{AC} = J_{BC} = 1.7$ cps.

In the spectrum of compound E two of the methyl signals appear as sharp singlets on irradiation of the olefinic signal at $\tau = 4.10$ (see fig. IV-4b). The third methyl signal is still broadened. Since it is assumed, that coupling of the allylic protons with methyl protons is only possible if the methyl group is situated at the ring positions 2 or 3, the broadened signal is ascribed to such a methyl group. The sharpened methyl signals are ascribed to methyl groups in 1- or 4-positions. The methyl signal at $\tau = 8.06$ showed without decoupling a doublet structure (J = 1.7cps). Therefore this signal is ascribed to the methyl group at the tri-substituted double bond of the CPD ring.

fig IV-4 NMR spectrum of 1.2.4.-TMCPD

a Without irradiation

b Irradiation of the olefinic proton

c Irradiation of one of the olefinic methyl groups

d Irradiation of the allylic protons

e Irradiation of one of the olefinic methyl groups

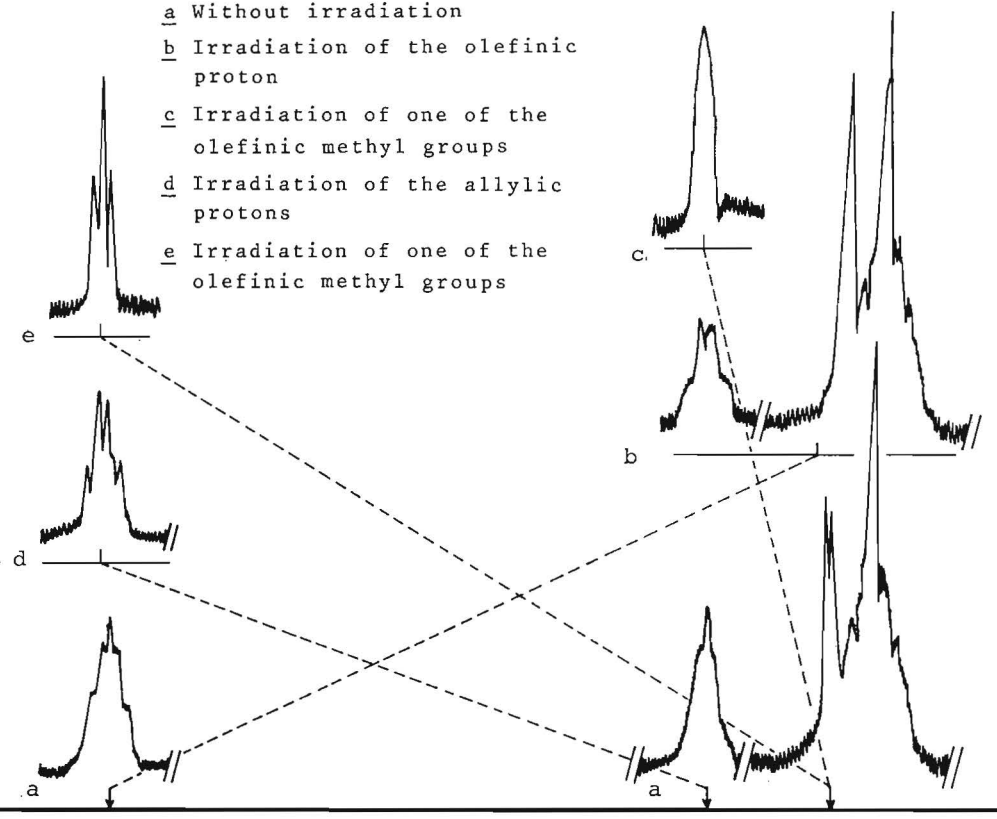
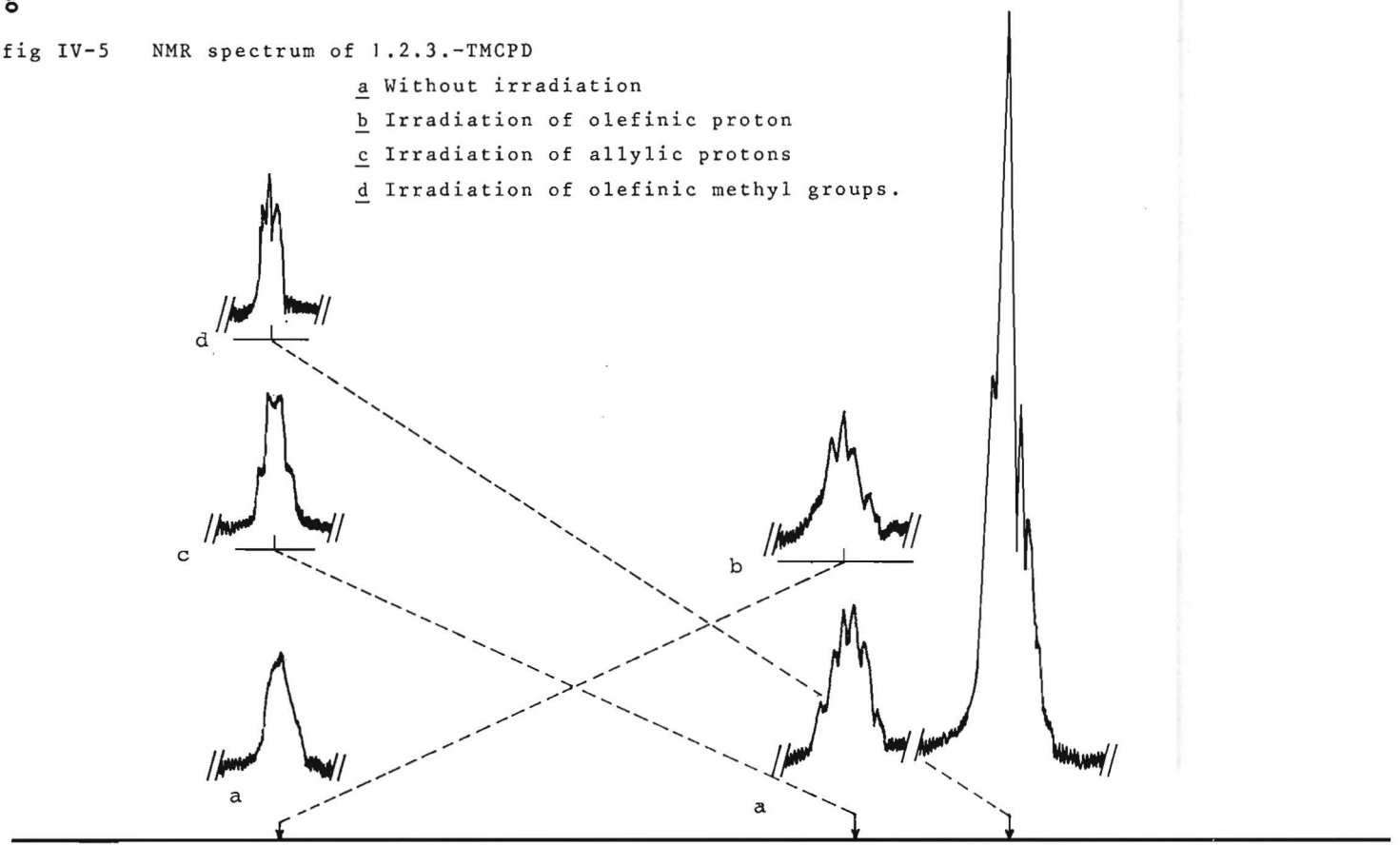


fig IV-5 NMR spectrum of 1.2.3.-TMCPD

a Without irradiation
b Irradiation of olefinic proton
c Irradiation of allylic protons
d Irradiation of olefinic methyl groups.



The allylic proton at C_5 couples with the olefinic proton and with one of the methyl groups (see before). The allylic multiplet appears as a regular quintuplet. This structure might result in this case from a combination of a quadruplet and a doublet splitting with equal spacings. On irradiating the methyl signals the allylic signal collapses to a close-spaced doublet (J = 1.7 cps, see fig.IV-4c). On irradiating the olefinic signals at τ = 4.10 a clearly recognisable quadruplet is observed for the allylic resonance (J = 1.7 cps, see fig. IV-4b).
The olefinic multiplet pattern was analysed in a similar way. It reduces to a sharp triplet (J = 1.7 cps) on irradiating the methyl signals and to a sharp quadruplet (J = 1.65 cps) by irradiation of the allylic resonance.In the spectrum of compound F the allylic resonance at τ = 7.28 is an octet with binomial intensity ratios. This structure results from equal couplings of the allylic protons with the olefinic proton and with the protons of the methyl groups at the positions 2 and 3 of the CPD ring.

This hypothesis has been substantiated by decoupling experiments. Hence irradiation of the olefinic signal at τ = 4.14 hardly changes the total signal width at τ =7.28 but one central line clearly comes to the fore as required for a heptet with the same spacings as the original octet (see fig. IV-5b). Irradiation of the methyl signals results in an appreciable narrowing of the allylic signal.
The olefinic pattern is again composed of a quadruplet and a triplet splitting of the same order, in close analogy with the spectrum of compound E.

It was shown by mass-, ultraviolet- and infrared spectrometry, that the four main thermolysis products of isobornylacetate are hydrocarbons C_8H_{12}, containing two conjugated double bonds. Hydrogenation of the two low-boiling compounds yielded 1.1.3.-TMCPD and 1.1.2.-TMCPD. Since neither from IR nor from NMR spectra indications were found for the presence of exocyclic double bonds,the structures 2.5.5.-TMCPD and 1.5.5.-TMCPD respectively could be assigned to these hydrocarbons. Hydrogenation of the higher boiling compounds yielded mixtures of isomeric

1.2.4.-TMCP's and 1.2.3.-TMCP's. There were again no indication for exocyclic double bonds. It was concluded from the NMR spectra that in both compounds all methyl groups are attached to double bonds. Therefore the structures 1.2.4.-TMCPD and 1.2.3.-TMCPD respectively were assigned to the high-boiling thermolysis products.

By infrared spectrometry only the pair of low-boiling products could be distinguished from the pair of high-boiling products and vice versa. In the NMR spectra of the low-boiling isomers different chemical shifts were found for the methyl groups. These differences were correlated to the molecular structures, using McConnel's formula. A confirmation of the structures of the high-boiling compounds was obtained from a detailed study of the allylic and olefinic spin multiplet patterns by means of double resonance.

From a more detailed consideration of the UV spectra and comparison of the results with those of CSICSERY (ref 42) the conclusion could be drawn that hypsochromic and batochromic shifts, caused by methyl substitution at the various ring positions, are additive.

IV-4 Structures of some side products.

During the preparation of the TMCPD isomers it became clear, that still some impurities are present in the"pure" compounds. (see also III-2).

Two kinds of possible contaminants will be considered here:

I) 1.2.4.-TMCPD and 1.2.3.-TMCPD (compounds E and F respectively) can isomerise by H-shifts to 1.3.5. -TMCPD + 2.3.5.-TMCPD and to 1.2.5.-TMCPD + 1.4.5.-TMCPD respectively (see also III-3).

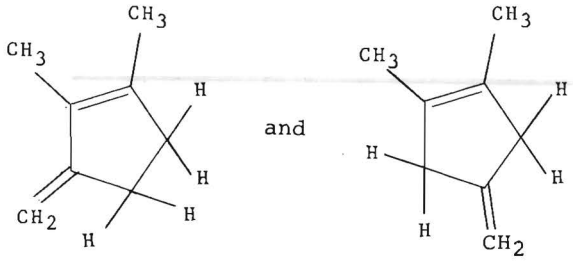
II) Three of the four TMCPD's apparently rearrange to compounds with exocyclic double bonds.

In the spectra of E and F weak signals are observed in the τ = 8.8 - 9.0 region, characteristic of methyl groups, attached to the allylic C_5 position of a CPD ring. The corresponding allylic and olefinic proton signals are not

detected since they are hidden under the spectra of the main compounds. A sample, rich in compound F was prepared by high temperature thermolysis of isobornyl acetate. This particular sample showed stronger absorptions in the τ = 8.8-9.0 region of the NMR spectrum. The IR spectrum showed five absorptions in the out-of-plane deformation region: at 717, 728, 772, 823 and 858 cm^{-1}. After heating for ½hr at 90°C, the bands at 772 and 823 cm^{-1} had almost disappeared, after 3 hrs also the 717 cm^{-1} band was absent.
MIRONOV et al (ref 23) prepared a mixture of 1.4.5.-TMCPD and 1.2.5.-TMCPD by careful distillation of an equilibrium mixture of the three vicinal TMCPD's. The IR spectrum of the distillate showed absorptions at 717, 772 and 823 cm^{-1}. The residue, 95% pure 1.2.3.-TMCPD, absorbed at 728 and 858 cm^{-1}. Heating of a non-equilibrium mixture invariably resulted in the formation of the mixture, containing 95% of the 1.2.3.-isomer. We may therefore conclude that the mixture, described above also contained the same H-shift contaminants.

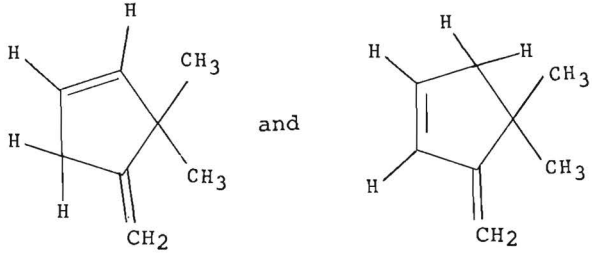
II. With respect to the contaminants mentioned under II: a) The mass spectra gave no indications for the presence of compounds with molecular weights different from that of the parent compounds. b) On hydrogenation the rearrangement products are converted to the same TMCPD's as the main components. Hence the isomerisations very likely do not involve skeletal rearrangements but only shifts of the double bonds, resulting in the formation of exo-methylene cyclopentene derivatives.
In samples of compounds A and B the concentrations of the impurities, A' and B' respectively, amounted to about 10%. No such impurity was found in 1.2.4.-TMCPD (compound E). In 1.2.3-TMCPD (compound F) the concentration rose to about 30% by heating in a glass ampoule (see III-3).
The NMR spectrum of this last mentioned impurity shows a broad signal at τ = 5.32, representing two protons and a signal of about twice that area at τ = 7.54. The original methyl signal of compound E was somewhat distorted, due to the presence of signals of the impurity. No signals are found above τ = 8.5. It follows from these data, that the impurity possesses one exocyclic double bond, four

allylic protons and that both methyl groups are connected to the endocyclic double bond . Thus the following two structures have to be considered:



The latter structure is ruled out by the hydrogenation results since it was shown that no skeletal isomerisation had occurred (see before). The presence of the exocyclic double bond is also evident from the IR absorptions at 3095 and at 882 cm^{-1}.

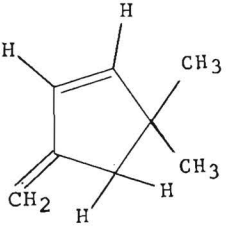
The spectra of compound B' has four signals at τ = 5.12, 5,34, 7,60 and 8.88 with relative intensities 1:1:2:6 respectively. The first two signals are ascribed to protons of an exocyclic double bond. This was substantiated by IR spectrometry: bands at 3098 and 893 cm^{-1}. The presence of only two allylic protons (τ = 7.60) indicated, that the methyl groups are attached both to allylic ring positions. Finally it is evident from the spectra that the two methyl groups are attached to the same ring carbon atom (sharp singlet structure at τ = 8.88). On the basis of these data the following structures are to be considered:



In both configurations the two protons at the exocyclic double bond are magnetically non-equivalent because of different shieldings experienced from the methyl groups.

In the former structure this effect will be overbalanced by the shielding of the ethylenic bond. The observed non-equivalence, 0.22 ppm, is rather large, pointing to the first-mentioned structure. In both configurations the signals would be broadened slightly by coupling with olefinic or allylic protons.

The spectrum of compound A' shows signals at τ =5.15, 7.63 and 8.90. The signal at τ = 5.15 is rather broad and represents two protons. The two other signals represent two and six protons respectively. In this case only one di-methyl-methylene-cyclopentene isomer has the correct skeletal structure:



The extra broad methylene signal is caused by coupling with the two endocyclic olefinic protons and the two allylic protons. The presence of the exoxyclic double bond is again substantiated by the appearance of the appropriate IR absorptions at 3095 and 892 cm^{-1}.

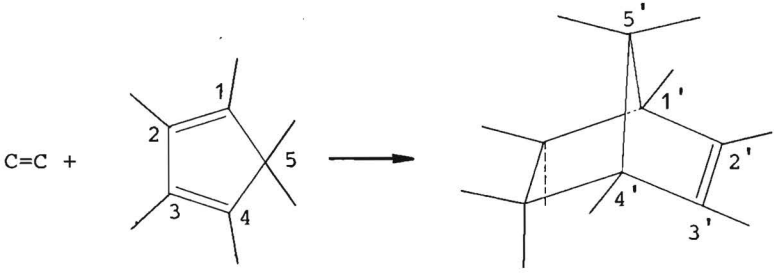
CHAPTER V

FORMATION AND NMR STUDY OF SOME BRIDGED RING COMPOUNDS OF THE NORBORNENE TYPE

V-I Introduction

V-I-I Diels Alder reaction of TMCPD isomers

The so-called diene synthesis may be a useful tool in the assignment of structures to substituted cyclopentadienes. The reaction was applied for the first time in 1927 by DIELS and ALDER (ref 47). The reaction, with ethylene as the dienophylic agent, proceeds as follows:



Each C-atom position in the original cyclopentadiene ring corresponds in a defined way with a C-atom position in the bicyclo-(221)-heptene-2 skeleton. (The positions of the C-atoms in the bicyclo-skeleton can be distinguished much better than in the original CPD derivatives). The degree of substitution of the 2'-3' ethylenic bond in norbornene can be deduced from the IR spectrum. This corresponds to the substitution of the 2- and 3-positions in the CPD ring. In the NMR spectra the different positions of the norbornene molecule: olefinic, bridgehead and bridge are clearly distinguishable. The same is true for methyl substituents as these all have different chemical shifts in the various positions.

Alternative dienophyles in the Diels Alder reaction of CPD would be e.g. vinylacetate or maleic anhydride. Both have the advantage over ethylene that the addition proceeds at

room temperature in the liquid phase, whereas ethylene addition requires more drastic conditions.
The main reason to take ethylene was, that a number of reference compounds was easily available by dehydration of fenchyl- and bornyl alcohol to fenchenes. Of course, application of the diene synthesis as a means of structure confirmation is only of value if no isomerisation reactions occur during the synthesis. ALDER and ACHE (ref 20) observed, that convenient reaction rates are obtained only at temperatures well above 100°C. A temperature of 250°C

and an ethylene pressure of 150-200 atm were found to be a good compromise. The reaction time was about one hour. Under such conditions compounds E and F are known to undergo H-shift isomerisations rapidly. So in fact "E" and "F" consist of thermodynamical equilibrium mixtures of possible H-shift isomers. This means, that in each case at least three adducts can be formed. If the Diels Alder reaction rates are of about the same order of magnitude for each of the H-shift isomers and also large compared with the H-shift isomerisation rates, than the predominating adducts in the reaction product mixtures will correspond to E and F respectively. If not, the main addition product will correspond to that H-shift isomer, which has the largest addition rate in the diene synthesis. ALDER and ACHE found, that norbornene derivatives also undergo thermal rearrangement reactions (ref 20). (see chapter II). To suppress isomerisations, the temperatures were kept between 100°C and 140°C in this work. Under these conditions only the H-shift isomerisations still occur. Isomerisation of compound A to compounds E and F makes it rather difficult to use the reaction in the case of compound A. Compound B rearranges only at temperature around 160°C. (see III-3).

V-1-2 NMR-study of bridged ring compounds

The second part of this chapter deals with the interpretation of the NMR spectra of a number of tri-methyl-norbornene derivatives. The study of such compounds in this work has a twofold purpose:

1) Correlation of the NMR spectra with the molecular structures and vice versa. In the early days of terpene chemistry the structures of some of the fenchenes and related compounds have been determined by chemical methods only. (For details the reader is referred to ref 48 .) More recently also IR spectrometry has been introduced as a tool in the structure elucidation (ref 39) of this class of compounds. It has been used e.g. to determine the degree of substitution of the double bond. Further the presence of a cyclopropane ring in tricyclic compounds can be read from the spectrum.
IR spectrometry is less suited for the determination of details like exo/endo and syn/anti isomerism. Since the structures are rigid, NMR spectroscopy was thought to be of more use. The fenchenes, the structures of which are well established, were used in this study to correlate the NMR spectroscopical data with the structures. Since the structures are rigid, all parts of the molecules remain in fixed positions relative to each other. Therefore these compounds provide excellent objects for the study of phenomenae, which are dependent on the relative positions of protons and for instance C=C and C-C bonds(refs49-55). With molecules, which contain hetero groups too many variables are usually involved to enable a straightforward correlation between chemical shifts and all the shielding influences and inductive effects. In tri-methyl-norbornenes the differences are caused mainly by the C=C,C-C and C-H bond anisotropies, the inductive effects of the methyl groups being rather small. In the following discussion of the NMR spectra of the fenchenes a few of the above mentioned phenomenae will be demonstrated on a qualitative way.

2) Structure determination of some Diels-Alder adducts of ethylene and TMCPD isomers of unknown structures, with the aid of NMR spectroscopy, using the experience, obtained in the NMR analysis of the fenchenes. Conversely, the structures of the TMCPD isomers can be deduced from the structures of the adducts.

V-2 Experimental and results

V-2-1 Diels Alder syntheses

All addition reactions were performed in a 250 cc Baskerville autoclave. Inside a glass capsule was placed enabling the handling of quantities of 1 cc with losses of not more than 10%. The temperature was reached within half an hour in each of the experiments. After 4 hrs the heating was switched off. The ethylene pressure was maintained for another 20 hrs.

Using a mixture, containing 75% compound E and 20% compound F, a number of trial experiments were carried out to find the optimal reaction conditions for avoiding isomerisation reactions. These conditions turned out to be:

temperature 130°C.
ethylene pressure 80-150 atm.
reaction time about 4 hrs.

The reaction product mixtures were analysed by GLC on packed as well as on capillary columns. The mixtures, resulting from the trial experiments consisted for about 65% of an adduct with a boiling point of approximately 141°C and for about 20% of a compound with a boiling point of approximately 151°C. These boiling points were estimated from the retention times of the compounds on an Apiezon column with the fenchenes as a series of reference compounds, and may be as good as ± 1°C. Finally the components of the reaction mixture were isolated by preparative gaschromatography. The major component (65%, 141°C) turned out to be identical with the product, obtained by taking 95% pure 1.2.4.-TMCPD ("E") as the starting compound. The mass-spectrum indicates a molecular weight of 136, in accordance with a molecular formula $C_{10}H_{16}$. The IR spectrum shows an absorption in the C=C stretching region at 1622 cm^{-1}. Only a weak band is observed at 3075 cm^{-1} and a medium intensity band at 800 cm^{-1}. These data point to the presence of a tri-substituted ethylenic bond in the bicycloskeleton as is evident from a comparison of the IR-spectrum with those of a number of fenchenes (ref 39). An olefinic resonance signal, corresponding with only one proton is found in the NMR spectrum.

Furthermore one of the methyl groups gives its resonance at about τ = 8.3 (doublet, J =1.7 cps), indicating that this methyl group is attached to the double bond. Finally a signal near τ = 8.7, representing six protons proves the existence of two bridgehead methyl groups (see also V-4). On the basis of the above data, the 1.2.4.-tri-methyl-norbornene structure is assigned to this adduct. This compound has not been described in the literature before.

In a similar way the minor compound (20%, 151^{0}C) was formed again by starting from 85% pure 1.2.3.-TMCPD ("F"). The mass spectrum reveales again a molecular weight of 136. In the IR spectrum an absorption is noticed at 1663 cm^{-1}, pointing to the presence of a tetrasubstituted double bond (ref 39). This is also consistent with the absence of C=C-H stretching absorptions near 3075 cm^{-1} and of the out-of-plane deformation mode in the 800-900 cm^{-1} region. The NMR spectrum shows the presence of one bridgehead methyl group (τ =8.7) and of two methyl groups, attached to the double bond (τ =8.25). No olefinic proton signals are found. Therefore the 1.2.3.-tri-methyl-norbornene structure is assigned to this adduct.

After treating 1.5.5.-TMCPD in the same way only 1.2.3.-TMCPD and its adduct are found apart from unreacted starting material. Therefore it was decided to lower the temperature to about 105^{o}C. The reaction time had to be increased since after 4 hrs the conversion was only 10%.This was raised to 50% after 24 hrs. Along the walls of the glass capsule a white solid was found which after analysis turned out to be the expected 1.5.5.-adduct bornene.

The mass spectrum of the adduct indicates a molecular weght of 136. In the IR spectrum evidence is found for the presence of a disubstituted double bond.The C=C stretching absorption is found at 1580 cm^{-1}, relatively strong absorptions are found near 3075 cm^{-1}, in accordance with the presence of one or two olefinic protons. This is consistent also with the strong absorptions in the out-of-plane deformation region near 820 cm^{-1}. The NMR spectrum shows the presence of two olefinic protons (τ = 4.1), one bridgehead methyl group (τ = 8.9) and two bridge methyl

groups (τ = 9.14, 9.20). On the basis of the above mentioned data the 1.7.7.-tri-methyl-norbornene structure is assigned to this adduct.

V-2-2 Preparation of the fenchenes by dehydration reactions.

Acid-catalysed dehydration of fenchyl- and bornyl alcohol was chosen for the preparation of the fenchenes. Fenchyl alcohol or derivatives should, without rearrangements, yield exclusively cyclofenchene while isofenchyl derivatives may yield cyclofenchene and δ-fenchene. Previous investigations have shown, however, that in no case the reaction proceeds smoothly and without rearrangements. The nature of the products, obtained by dehydration of fenchyl alcohol under various conditions have been studied comprehensively by TOIVONEN, by KOMPPA and NYMAN and by PULKKINEN (refs 56,57,58).500 ml fenchyl alcohol and 150g$KHSO_4$ were mixed. A mixture of water and fenchenes was distilled off continuously while the temperature was raised gradually from 150°C to 180°C. The distillate was neutralised with sodium carbonate solution and washed several times with water. Finally it was dried over anhydrous calcium chloride.

The hydrocarbon mixture was analysed by GLC on a 4m Apiezon column at 100°C. The composition was:

1.5.5.-tri-methyl-norbornene	(δ-fenchene)	5%
2.5.5.- "	(γ-fenchene)	20%
2.7.7.- "	(ξ-fenchene)	
1.2.3.- "	(ε-fenchene)	50%
1.3.3.-tri-methyl-tri-cycloheptane	(cyclofenchene)	20%
2-exo-methylene-5.5-di-methyl-norbornane	(β-fenchene)	20%
2-exo-methylene-3.3-di-methyl-norbornane	(camphene)	25%

Treatment of bornyl alcohol in the same way yielded a mixture of about 20% 1.7.7.-tri-methyl-tricyclo-(2210)-heptane (tricyclene) and 80% 2-exo-methylene-3.3-di-methyl-norbornane (camphene). The fenchene mixture was distilled in a Podbielniak column (about 70 t.p.) at atmospheric

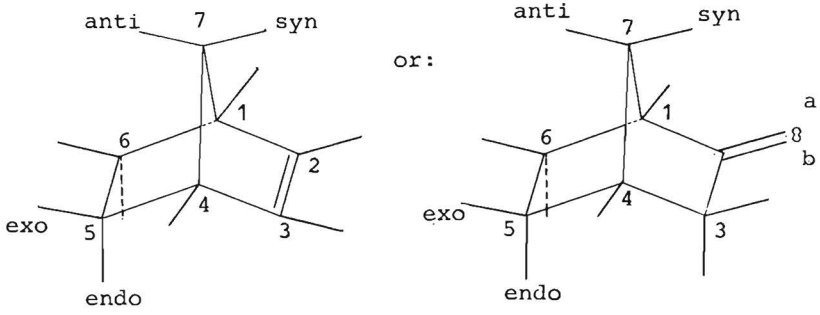
pressure. A distillation curve, analogous to that of PULKKINEN (ref 58) was obtained. From two fractions, rich in δ-fenchene and cyclofenchene respectively, these two compounds were isolated by preparative chromatography (7m Apiezon at 140°C), the other compounds did not survive such a preparative GLC purification with the exception of camphene. In most cases an equilibrium mixture was formed, containing cyclofenchene and camphene as the major components. Presumably the support of the preparative columns stationary phase acted as an acid catalyst. The other isomers were therefore purified further by repeated injection of 8 μl fractions in a normal analytical column (4m Apiezon). Tricyclene and β-fenchene were prepared in this way. γ-Fenchene and ξ-fenchene have identical retention times on an Apiezon column. For this reason only a mixture was obtained, containing approximately 65% γ-fenchene and 35% ξ-fenchene. β- and γ-fenchene are so poorly separated, that only very minute amounts of the latter were isolated. Its presence in the distillation fractions was decuced from the IR spectra (bands at 776 cm^{-1} and 733 cm^{-1}). 1.2.3.-tri-methyl-norbornene decomposed obviously during the distillation process since it was not found back in the distillate.

The IR spectra of all compounds were run on a Perkin Elmer 237 instrument, using carbon tetrachloride solutions between 4000 cm^{-1} and 900 cm^{-1} and carbon disulfide solutions for the 900-650 cm^{-1} region. As far as the spectra had been published previously, our results are in agreement with those of the previous investigators. (refs 39,58). For the unknown compound 1.2.4.-tri-methyl-norbornene the degree of substitution of the double bond is deduced from the IR spectrum by comparison with the spectra of the other isomers.

V-3 Analysis of the NMR spectra.

The chemical shifts and coupling constants in each of the fenchenes will be given now. For convenience this will be done for each of the compounds separately. Coupling constants and chemical shifts in norbornene are known from

the work of SNYDER and FRANZUS and of LASZLO and von RAGUÉ SCHLEYER (refs 49,50). The syn-bridge proton is found at the highest field. The anti-bridge proton resonance is recognised from its spin coupling pattern. For the rest of the spectrum the following sequence in chemical shifts is found: $\tau_{olef} < \tau_{bridgehead} < \tau_{exo} < \tau_{endo}$. As the chemical shifts of the methyl groups are generally determined by the same factors as the corresponding protons, the same sequence in chemical shifts is assumed for the methyl substituents in this study. The numbering in the bicyclic skeletons is as follows:



Compounds 1 - 8 were prepared by dehydration of fenchyl- and bornyl alcohol (see V-2-2). Hydrogenation of γ-fenchene and camphene yielded compounds 9-12. Compounds 13-15 were obtained by Diels Alder additions of the corresponding TMCPD derivatives and ethylene (see V-2-1). The structures of these last three compounds are confirmed among other things by comparison of their NMR spectra with those of the compounds 1 - 8 (see V-I, 2). Details of the various spectra are now given. The chemical shifts are summarised in table V-I.

I) 1.5.5.-tri-methyl-norbornene (δ-fenchene).

The protons 7-syn and 7-anti form an AB type quadruplet (J = 11 cps) with the syn-part further splitted into doublets with J = 2.4 cps by coupling with H_4. Irradiation of the bridgehead proton signal at τ = 7.78 results in a simple AB quadruplet in the olefinic region of the spectrum: J_{23} = 6.3 cps. Double resonance experiments showed that $J_{27_a} = J_{37_a}$ = 0.6 cps. Irradiation of the olefinic resonance results in a narrowing of about 3.3 cps for the

Table V-1 Chemical shifts in tri-methyl-norbornenes

	C_1		C_2 (or C_{8a})		C_3 (or C_{8b})		C_4		C_5				C_6		C_7			
									exo		endo		exo	endo	syn		anti	
Comp. no.	H	Me	H	Me	H	Me	H	Me	H	Me	H	Me	H	H	H	Me	H	Me
1)	----	8.75	4.14	----	3.86	----	7.78	----	----	8.81	----	9.13	±8.6	±9.0	±9.1	----	±8.4	----
2)	7.84	----	----	8.26	4.29	----	7.84	----	----	8.82	----	9.12	±8.2	±8.6	±9.1	----	±8.6	----
15)	----	8.94	4.26	----	3.96	----	7.69	----	±8.4	----	±8.8	----	±8.4	±8.8	----	9.20	----	9.14
3)	7.52	----	----	8.26	4.46	----	7.52	----	±8.2	----	±8.6	----	±8.2	±8.6	----	9.13	----	9.03
13)	----	8.76	----	8.32	4.40	----	----	8.72	±8.2	----	±8.6	----	±8.2	±8.6	±8.9	----	±8.6	----
14)	----	8.73	----	8.36	----	8.26	7.42	----	±8.2	----	±8.6	----	±8.2	±8.6	±9.0	----	±8.6	----
7)	----	8.77	9.0	----	?	----	8.13	----	----	9.08	----	9.12	±9.0	±9.0	±9.4	----	±9.2	----
8)	----	8.97	8.8	----	?	----	8.16	----	±8.4	----	±8.7	----	±8.8	±8.8	----	9.16	----	9.16
9)	8.08	----	----	exo 8.92	?	----	8.08	----	----	8.96	----	9.02	?	?	?	----	?	----
10)	8.07	----	----	endo 9.03	?	----	8.07	----	----	8.99	----	9.04	?	?	?	----	?	----
11)	8.00	----	----	exo 9.00	?	9.03 9.10	8.00	----	?	----	?	----	?	?	?	----	?	----
12)	7.98	----	----	endo 9.17	?	9.05 9.19	7.98	----	?	----	?	----	?	?	?	----	?	----
4)	7.39	----	5.17	----	5.37	----	7.79	----	8.06	----	8.30	----	±8.5	±8.7	?	----	±9.1	----
5)	?	----	5.25	----	5.42	----	?	----	?	?	?	?	?	?	----	9.0	----	9.2
6)	7.33	----	5.27	----	5.49	----	8.10	----	----	8.94	----	8.96	?	?	?	----	?	----

bridgehead signal, the effect being about the sum of J_{24} and J_{34}. From J_{47_s} = 2.4 cps and assuming an intrinsic line width of about 0.4 cps, it is deduced that:

$$J_{47_a} = 5.3 - 0.4 - 2.4 = 2.5 \text{ cps.}$$

since the actual line width is 5.3 cps. J_{47_a} and J_{47_s} have identical values within experimental error.

2) 2.5.5.-tri-methyl-norbornene (γ-fenchene).

The olefinic signal is rather broad, no details are visible. The total line width is given by:

$$(3J_{38} + J_{34} + J_{13} + J_{37_a} + 0.4) \text{ cps.}$$

J_{38} is determined from the doublet structure of the methyl signal at τ = 8.26 : J_{38} = 1.8 cps. J_{34} is known to be about 3 cps (see also compounds nos 1 and 15), J_{13} is estimated at 0.5 cps (ref 49) and J_{37_a} at 0.5 cps. Thus the total band width is calculated at:

$$3 \times 1.8 + 3.0 + 0.5 + 0.5 + 0.4 = 9.8 \text{ cps.}$$

Actually just over 10 cps is found experimentally. These values were substantiated partially by irradiation of the bridgehead proton signal and of the methyl signal at τ= 8.26, yielding a narrowing of 3.0 and 5.4 cps respectively. The width of the signals of the bridgehead protons cannot be reconstructed in a similar way since they are in principle non-equivalent, both with respect to chemical shift as to coupling with neighbouring protons.

3) 2.7.7.-tri-methyl-norbornene (ξ-fenchene).

For the olefinic proton signal a similar calculation as for γ-fenchene can be made the only difference being the occurence of $J_{35_{exo}}$ instead of $J_{37_{anti}}$. In practice a similar line width as for γ-fenchene is measured. For the bridgehead protons again the same difficulties as for γ-fenchene are encountered.

4) 2-exo-methylene-5.5-di-methyl-norbornene (β-fenchene).

The two exo-methylene protons, H_{8_a} and H_{8_b} are non-equivalent. It is known from non-cyclic olefins that $J_{8_a 8_b}$ =

0.5 cps. The signals are however broadened by coupling with the C_3 -protons. The spectrum between τ = 7.4 and τ = 8.9 is very complicated, $\tau_{3_{exo}}$ and $\tau_{3_{endo}}$ have been obtained by double resonance. It turned out that $J_{3_{exo}8}$ = $J_{3_{endo}8}$ = 2.8 cps and that J_{18} = 0.5 cps. The total width of the signal of the protons at C_8 is:

$$2J_{38} + J_{18} + 0.4 = 6.5 \text{ cps.}$$

This is not in agreement with the experimental value: 7.5 cps. Probably the extra broadening might be due to some long range coupling with protons at C_1, C_6 or C_7. This was however not substantiated by double resonance experiments. The H_4-signal appears as a regular quintuplet (J = 2.5cps). This may result from equal couplings with the protons at C_3 and C_7 .This assumption is substantiated by irradiating at τ = 8.06, 8.30 and 9.10 which results each time in a quadruplet (J = 2.5 cps).

5) 2-exo-methylene-7.7-di-methyl-norbornene (α-fenchene).

A spectrum was run of a mixture, containing 35% of α -fenchene, the remaining 65% being β -fenchene and camphene. Therefore not many details were observed. The exo-methylene signals are about as broad as in β -fenchene.

6) 2-exo-methylene-3.3-di-methyl-norbornene (camphene).

The methylene protons 8a and 8b appear as relatively sharp singlets. The rest of the broadening is caused by coupling with the proton at the bridgehead position at C_1 as is shown by double resonance (irradiation at τ = 7.33). The bridgehead proton resonance at τ = 7.33 is broadened by $J_{16_{exo}}$ (=3 cps) and by $J_{17_{anti}}$ = $J_{17_{syn}}$ = 2.3 cps(shown by double resonance).

7) 1.7.7.-tri-methyl-tricyclo-(2210)-heptane (tricyclene).

In this compound all chemical shifts are very much alike: the whole spectrum is compressed in an area of 1 ppm. The double resonance technigue therefore is of little value, the more since most protons are coupled strongly.

8) 1.3.3.-tri-methyl-tricyclo-(2210)-heptane (cyclofenchene).

The same difficulties as with tricyclene are encountered in analysing the spectrum. Moreover it is extra complicated with respect to tricyclene by the loss of symmetry. New signals are found at high fields. They are ascribed to the bridge protons.

9-12 Exo/endo-2.5.5./2.3.3.-tri-methyl-norbornene.

Not many details are observed as a consequence of the nearly identical chemical shifts and the large coupling constants, The bridgehead proton resonances are broader than might be expected from a consideration of the appropriate coupling constants. Therefore it is concluded that H_1 and H_4 are not completely equivalent. The methyl group at C_2 is easily recognised from its doublet structure by coupling with H_2 (J = 6.7 cps). Chemical shifts of methyl groups and of bridgehead proton signals' are given in table V-I.

13) 1.2.4.-tri-methyl-norbornene.

The olefinic spin multiplet is not distorted by coupling with bridgehead protons. By double resonance the values J_{38} = 1.8 cps, J_{37anti} = 0.5 cps and J_{35exo} = 0.5 cps were obtained.

14) 1.2.3.-tri-methyl norbornene (ε-fenchene).

The bridgehead proton resonance is broadened by coupling with the protons at C_7 and C_5. The total band width is:

$$J_{47a}+J_{47s}+J_{45exo}+J_{45endo}+ 0.4 = 2.1+2.1+3.2+0.4+0.4=8.2cps.$$

A band width of about 8.5 cps is found experimentally. This is reduced to 4.5 cps by irradiation at τ = 8.9(thus cancelling J_{47a} and J_{47s}). The signals of the olefinic methyl group are broadened (6cps) by mutual coupling J = 1.7 cps.

15) 1.7.7.-tri-methyl-norbornene (bornene).

The spin coupling pattern in the olefinic region is very similar to that of δ -fenchene (No. 1). Spin decoupling yielded: J_{23} = 5.1 cps, J_{34} = 3.1 cps and J_{24} = 0.6 cps. The longe range couplings J_{25exo} and J_{36exo} are shown to be about 0.4 cps. The bridgehead proton resonance is formed by a triplet, resulting from approximately equal couplings with H_3 and H_{5exo}: $J_{34} = J_{45exo}$ = 3.1 cps. The extra broadening is attributed to J_{24}. Irradiation of the olefinic part yielded that J_{45endo} = 0.5 cps. The pattern of the exo- and endo-protons at C_5 and C_6 could not be analysed completely. Most probably all chemical shifts are different by the action of the bridgehead methyl groups. Moreover , all spins are coupled strongly.

Alcohols and acetates

The NMR spectra of the bicyclic alcohols: fenchol, borneol and of the corresponding acetates have not been analysed completely. The signal of H_2 is easily recognised since it is generally found at the lower field side of the spectrum. Chemical shifts as far as determined, are given in table V-2.

Table V-2 Some τ-values in bicyclic alcohols and acetates

Compound	τ_2	τ_{OH}	τ_{acet}	$\tau_{methyl\ groups}$		
Isoborneol	6.37	7.27	----	8.98,	9.11,	9.17
Borneol	5.93	7.22	----	9.12,	9.12,	9.15
Fenchol	6.74	7.64	----	8.91,	9.01,	9.14
Isobornyl acetate	5.25	----	8.03	9.00,	9.16,	9.16
Bornyl acet	5.02	----	7.98	9.05,	9.11,	9.16
Fenchyl acet	5.60	----	7.97	8.88,	8.94,	9.22

V-4 Discussion of the NMR spectra

In this discussion the tri-methyl-norbornanes are denoted by the letter combination TMNBA, the norbornene derivatives by TMNBE, thus δ-fenchene (1.5.5.-tri-methyl-norbornene) = 1.5.5.-TMNBE. Tri-methyl-tricyclo-heptanes are referred to as TMTCH.

Several remarkable differencesin chemical shifts are found between corresponding protons in norbornene and in trimethyl-norbornene derivatives. The differences between the various isomers must be attributed to the different positions of the methyl groups. These effects can in principle be calculated from McConnell's formula. The values of r and θ were evaluated from a Dreiding model of bicyclo-(221)-heptene-2 in which the C_7 atom is represented by a C-atom, used in four-membered rings. It is known, that for distances less than 3-4 A too small shielding values are calculated (ref 44). Therefore only the sign and the order of magnitude of the chemical shift will usually be considered. The distortion of the original norbornene symmetry in 1.5.5.-TMNBE and 1.7.7.-TMNBE is evident from the chemical shifts of the olefinic proton signals (see table V-3). The proton H_2 in 1.5.5.-TMNBE has shifted 0.09 ppm to higher fields, compared to norbornene, whereas H_3 has shifted 0.09 ppm to higher fields, compared to norbornene, whereas H_3 has shifted downfield by about 0.21 ppm. A similar difference is found in 1.7.7.-TMNBE. An upfield shielding for H_2 of 0.07 ppm is calculated fromMcConnell's formula when the bridgehead proton at C_1 is replaced by a methyl group. The effect of the methyl groups at C_5 on H_2 is calculated to be about 0.02 ppm. The effect of the bridgehead methyl group upon H_3 is also very small. A diamagnetic shielding of 0.05 ppm by the C_5endo methyl group is calculated for H_3 against a paramagnetic shielding of 0.02 ppm by the C_5 exo methyl group.

Table V-3

Compound	τ_2	τ_3	$\Delta\tau$
Norbornene	4.07	4.07	---
1.5.5.-TMNBE	4.14	3.86	0.28
1.7.7.-TMNBE	4.26	3.96	0.30

An upfield shift of about 0.1ppm is found for the olefinic signals in 1.7.7.-TMNBE with respect to 1.5.5.-TMNBE (see table V-3). This difference is correlated to the replacement of the C_7 protons by methyl groups in 1.7.7.-TMNBE, The corresponding shielding influences on the olefinic protons are, according to McConnell's formula, +0.13 ppm

and -0.02 ppm for the syn- and for the anti-positions respectively. The replacement of the C_5 methyl groups by protons will only have a slight effect on H_3 (by about -0.02 ppm). This is reflected by the fact, that the upfield shift, going from 1.5.5.- to 1.7.7.-TMNBE is somewhat smaller for H_3 than for H_2. It is evident from the above mentioned data, that the signs of all differences observed are in agreement with the values, calculated theoretically from McConnell's formula. The downfield shift of 0.20 ppm for H_3 in 1.5.5.-TMNBE and 1.7.7.-TMNBE relative to norbornene are probably caused by some inductive effects of the bridgehead methyl group on the C_2=C_3 ethylenic bond.

The bridgehead proton H_4 is found at τ = 7.78 in 1.5.5.-TMNBE and at τ = 7.69 in 1.7.7.-TMNBE against τ = 7.15 in norbornene. The relative values in 1.5.5.-TMNBE and 1.7.7-TMNBE are again in agreement with the predictions. The large shift compared to norbornene cannot be explained in this manner. The displacement of the C_5 methyl groups to C_7 is also reflected by the upfield shift of the bridgehead methyl group at C_1 (+0.19 ppm). The sign and the order of magnitude are again correct.

Table V-4 Chemical shifts of bridgehead protons.

Compound(s)	τ_4-values	$\Delta\tau$
Nobornene	7.15	----
1.5.5.-TMNBE-1.7.7-TMNBE	7.78-7.69	-0.19
2.5.5.-TMNBE-2.7.7-TMNBE	7.84-7.52	-0.32
1.5.5.-TMTCH-1.7.7-TMTCH	8.13-8.16	+0.03

In 2.5.5.-TMNBE and 2.7.7-TMNBE only one bridgehead proton resonance is found, representing two protons. Displacement of the C_5 methyl groups to C_7 causes a downfield shift of -0.32 ppm, analogous to the case of 1.5.5.-TMNBE and 1.7.7.-TMNBE (see table V-4), in accordance with predictions. In β-fenchene and camphene two separate signals appear, due to the oppposite influences of the methyl groups and the exocyclic double bonds. In the saturated tri-methyl-norbornanes these signals are found at τ = 8.03 ± 0.05. In the tricyclic compounds an extra shift of

+ 0.10 ppm is probably caused by diamagnetic influence of the cyclopropane ring. (see table V-4).

Only part of the observed differences between the chemical shifts of methyl groups at the exo- and endo positions at C_5 in 1.5.5.-TMNBE and 1.7.7.-TMNBE is to be ascribed to the action of the double bond. The rest is caused by C-C and C-H bond anisotropies, analogous to the methyl substituted cyclohexanes (ref). This is evident from the fact, that still differences are found after hydrogenation of the double bonds. Exo methyl groups are shifted upfield by about 0.13 ppm whereas endo methyl groups are shifted downfield by about 0.08 ppm. HOOGEVEEN c.s. (ref 59) investigated the influence of hydrogenation upon exo- and endo protons at C_5 and C_6. For exo protons they observed a downfield shift of about 0.40 ± 0.25 ppm, while for endo protons a downfield shift of about 0.15 ppm was found. Applying McConnell's formula $\Delta\chi$-values were obtained from the almost constant upfield shifts, found for the bridgehead protons H_1 and H_4. After that the equation was used to calculate the effects for protons at C_5 and C_6.

Actually an upfield shift for exo protons of +0.27 ppm and a downfield shift for endo protons of -0.32 ppm were calculated. Similar considerations hold true for bicyclic compounds of the pinane type. Formerly the difference in τ -values between the two cyclobutane methyl groups in α-pinene have been attributed to the action of the double bond (ref 60). It has been shown, however, that similar shifts occur in β -pinene (= 0.50 ppm against 0.42 ppm in α-pinene) and in the saturated compounds cis-pinane and transpinane ($\Delta\tau$ = 0.19 ppm and 0.38 ppm respectively). The τ -differences between the C_7 methyl groups in 1.5.5.-TMNBE and 1.7.7.-TMNBE must be attributed exclusively to different shieldings by the double bond. In each of the compounds with an exocyclic double bond: camphene, β-fenchene and α -fenchene the characteristic exo/endo and syn/anti difference are not found: the two remaining methyl groups have almost indentical chemical shifts: τ = 8.94 + 8.96, 9.03 and 9.00 respectively. This is, however, not consistent with the 0.24 ppm difference, found for H_{3exo} and H_{3endo} in the spectrum of β -fenchene.

In bornane all three methyl groups are found at τ = 9.16 (ref 61). In 1.7.7.-TMTCH and 1.5.5.-TMTCH a cyclopropane ring is introduced by the formation of the extra C_2-C_6 bond. The chemical shifts of the bridge methyl groups are scarcely influenced (τ = 9.18). The bridgehead methyl group in 1.7.7.-TMTCH is obviously situated in the paramagnetic region of the cyclopropane ring since it has shifted downfield by about -0.20 ppm to τ = 8.97.In 1.5.5-TMTCH this group resonates at τ = 8.77. This extra downfield shift is attributed again to the displacement of the two methyl groups from C_7 to C_5. The magnitude of this effect is the same as for the corresponding norbornene derivatives 1.7.7.-TMNBE and 1.5.5.-TMNBE. (τ = 8.94 and 8.75 respectively). The relative shifts of the C_5 methyl groups in cyclofenchene, 0.04 ppm is similar to those in the two 2.5.5.-TMNBA's: 0.06 ppm for the exo isomer and 0.05 ppm for the endo isomer. The absolute values are larger in cyclofenchene by about 0.10 ppm, presumably by the influence of the cyclopropane ring.

Table V-5 Chemical shifts of C_5 methyl groups

Compound	τ_{exo}	τ_{endo}
1.5.5.-TMNBE	8.81	9.13
2.5.5.-TMNBE	8.82	9.12
1.5.5.-TMTCH	9.08	9.12
Exo -2.5.5.-TMNBA	8.96	9.02
Endo-2.5.5.-TMNBA	8.99	9.04
Exo -2.3.3.-TMNBA	9.03	9.10
Endo-2.3.3.-TMNBA	9.05	9.19

In the spectra of the 1.2.4.- and 1.2.3.-TMNBE only two kinds of methyl signals are observed: bridgehead methyl groups near τ = 8.7 and "olefinic" methyl groups near τ = 8.3. For the 1.2.4.-isomer two bridgehead methyl resonances are observed at τ = 8.72 and τ = 8,76,ascribed to the groups at C_4 and C_1 respectively. The double bond methyl group has shifted somewhat and is found at τ = 8.32. The sign of this shift (+0.06 ppm) and the order of magnitude are again in accordance with theory the same is true

for the corresponding upfield shift of the C_1 methyl group (+0.04 ppm). The olefinic proton signal is found at about the same field as in 1.5.5.-TMNBE.

In the spectrum of 1.2.3.-TMNBE a bridgehead proton signal is found at τ = 7.42 which is at lower fields than in most of the other isomers (see before). This is due to the absence of screening methyl groups at the 5- and 7-positions. The double bond methyl groups are not completely equivalent: τ = 8.26 and τ = 8.36 respectively. Therefore mutual coupling causes a broadening of the signal to about 6.5 cps.

Alcohols and acetates

The difference in τ -values between alcohols and acetates is attributed to different electron withdrawal powers of hydroxyl- and acetate groups. The influence of exo- and endo positions of H_2 can be seen from a comparison of the spectra of borneol and isoborneol and of the corresponding acetates: the proton at C_2-endo in isoborneol resonates at a 0.44 ppm higher field than the proton at C_2-exo in borneol (see table V-2). The corresponding difference in the acetates is 0.23 ppm.

In fenchol and fenchyl acetate the C_2-proton is shielded by the two methyl groups at C_3. The actual difference in τ -values for H_2 in fenchol and borneol is 0.81 ppm. (for the acetates the effect is 0.58 ppm, see table V-2). These effects are rather large to be ascribed only to different shieldings by the methyl groups as is evident from an application of McConnell's formula. Probably some steric hindrance effects are involved as well.The multiplicity of the H_2 signals in borneol, isoborneol and the acetates is governed by the following sets of coupling constants:

$J_{2exo3exo}$	= 10.0 cps	$J_{2endo3endo}$	= 7.5 cps
$J_{2exo3endo}$	= 3.8 cps	$J_{2endo3exo}$	= 4.0 cps
$J_{2exo6exo}$	= 1.8 cps	$J_{2endo6endo}$	= 0 cps

This couplings were calculated from the Karplus equation. The second set of coupling constants is easily recognised in borneol and bornyl acetate. In isoborneol and its acetate a semi-triplet structure is observed. This may re-

sult either from equal couplings with neighbouring protons or by equal chemical shifts of these protons (H_{3exo} and H_{3endo}). It has been shown, that change of solvent has sometimes different effects for the H_3 protons (ref 49), by which the triplet structure changes to a doublet of doublets. These results have been substantiated in this work by the use of spin-decoupling. For isobornyl acetate the complete triplet structure is removed by irradiating at τ = 8.15, indicating that $\tau_{3exo} = \tau_{3endo}$. Normally the exo- and endo protons are separated by about 0.4 ppm.Obviously the exo-acetate group shields H_{3exo} to such an extent, that almost identical τ -values are obtained.In bornyl acetate the secondary doublet splitting (J = 3.7 cps) is removed by decoupling at about τ = 8.85 while the primary coupling (J = 10 cps) is cancelled by saturating the signal at about τ = 7.90. The intrinsic $\Delta\tau_{(endo-exo)}$ is obviously accentuated extra by the specific shielding behaviour of the acetate group. In fenchol and fenchyl acetate the 3-position is occupied by two methyl groups. Thus $J_{2exo3exo}$ and $J_{2exo3endo}$ do not exist. According to FLAUTT and ERMANN (ref 62) and TORI c.s. (ref 61), the remaining doublet structure should be attributed to $J_{2exo6exo}$ (= 1.8 cps).

For H_{6exo} a τ -value of 8.6 to 8.7 is to be expected. The doublet structure is, however destroyed by irradiation at τ = 8.98 in fenchol and at τ = 8.92 in fenchyl acetate. These τ -values are rather high to be ascribed to H_{6exo}. Moreover, the observed J-value (1.2 cps) is considerably smaller than the value of 1.8 cps, given by previous investigators. The observed splitting is therefore ascribed to $J_{2exo7anti}$, in analogy to the norbornenes.

The methyl signals is isoborneol, borneol and the corresponding acetates have been assigned by TORI c.s.(ref 61). On the basis of previous results they reported, that the spacial vicinity of a hydroxyl and a methyl group causes a marked downfield shift for the methyl group whereas acetylation causes a characteristic upfield shift. In most of the 2-substituted norbornanes three distinct signals are found, corresponding to the three methyl groups.

Usually one of these groups signals is sharper and higher than the other two, characteristic of a less hindered methyl group. This signal is ascribed to the bridgehead methyl group on the basis of spectra, obtained for 1- and 7syn-substituted bornanes. The broader signals at higher fields are ascribed to the methyl groups at the 7anti- and 7syn positions respectively. The above mentioned "sharp signal rule" applies also to the hydrocarbons, studied in this work as is evident from the spectra of e.g. 1.5.5.-TMNBE, 1.7.7.-TMNBE, 1.7.7.-TMTCH and 1.5.5.-TMTCH. Therefore TORI's assignments are adopted in this study. The chemical shifts, measured here are generally in fair agreement with those of TORI with the exception of bornyl acetate where signals are found at τ = 9.05, 9.11 and 9.16 against respectively τ = 9.09, 9.13 and 9.17 in TORI's work. Following the same rule for fenchol and the acetate, the bridgehead methyl resonances are found at τ = 8.91 and τ = 8.94 respectively. The downfield shifts relative to the corresponding bornyl derivatives, -0.24 ppm and -0.22 ppm respectively are again in agreement with results, predicted by McConnell's formula when the bridge methyl groups are displaced to C_3 or C_5 (see before). The 3exo- and 3endo-methyl signals are found at τ = 9.01 and τ =9.14 in fenchol and at τ = 8.88 and τ =9.22 in fenchyl acetate. The large difference in the acetate is ascribed to the electronegativity and diamagnetic anisotropy effects of the acetate group.

SAMENVATTING

De thermische ontleding van fenchyl-, bornyl-, en isobornyl acetaat werd bestudeerd met behulp van twee typen doorstromingsreaktor bij temperaturen van 400°C tot 700°C. De reactiesnelheden werden gemeten in een microdoorstromingsreaktor-gaschromatograaf kombinatie. De berekende waarden voor de aktiveringsgrootheden bleken in goede overeenstemming te zijn met reeds eerder(o.a. door Scheer) bepaalde waarden voor de thermische ontleding van sekundaire acetaten.
Voor thermolyse op een preparatieve schaal werd gebruik gemaakt van een macrodoorstromingsreaktor (inhoud, afhankelijk van de gebruikte reaktorbuis, 250 tot 1000 cm^3). Enige thermolyseprodukten werden uit het mengsel geïsoleerd door middel van destillatie en preparatieve gaschromatografie.
Het bleek, dat een of meer van de primair door afsplitsing van azijnzuur ontstane $C_{10}H_{16}$ verbindingen reeds bij betrekkelijk lage temperaturen (≈ 450°C) een retro-Diels Alder reaktie ondergaan onder vorming van etheen en vier tri-methyl-cyclopentadiëen (TMCPD) isomeren. Bij zeer hoge temperaturen (600-700°C) werden in hoofdzaak aromaten gevonden.

De strukturen van de tri-methyl-cyclopentadiënen werden bevestigd door kombinatie van de resultaten verkregen met behulp van hydrogenering, massaspectrometrie, ultraviolet- en infrarood absorptie spektrometrie en kernmagnetische resonantie. De strukturen van de vier hoofdprodukten bleken te zijn: 2.5.5.-TMCPD, 1.5.5.-TMCPD, 1.2.4.-TMCPD en 1.2.3.-TMCPD.
De strukturen van een aantal zijprodukten werden op analoge wijze vastgesteld.

Bij de bestudering van de hierboven beschreven thermolysereakties ontstond de indruk, dat bij de retro-Diels Alder

reaktie de isomeren 2.5.5.-TMCPD en 1.5.5.-TMCPD de primaire produkten vormen, terwijl 1.2.4.-TMCPD en 1.2.3.-TMCPD worden gevormd door thermische isomerisatie van de beide eerstgenoemde isomeren. Om dit te bevestigen werd het thermisch gedrag van de beide geminale isomeren onderzocht zowel met de microdoorstromingsreaktor als door verhitting in glazen ampullen. Inderdaad konden bij deze onderzoekingen de reakties:

1.5.5.-TMCPD ⟵ 1.2.3.-TMCPD

en 2.5.5.-TMCPD ⟶ 1.2.3.-TMCPD + 1.2.4.-TMCPD

worden aangetoond. Deze reakties zijn analoog aan reeds bekende intramolekulaire "sigmatrope" verschuivingen van waterstofatomen en methylgroepen in ionen of, photochemisch en thermisch, in molekulen met twee of meer gekonjugeerde dubbele bindingen. Zij vormen het eerst bekende voorbeeld van een thermische 1 ⟶ 5 verschuiving van methylgroepen.

Additie van etheen aan tri-methyl-cyclopentadiënen resulteert in de vorming van tri-methyl-norbornenen.(fenchenen) De NMR spectra van deze verbindingen zijn interessant omdat de fencheenmolekulen zeer star zijn. Hierdoor is het betrekkelijk eenvoudig, chemische verschuivingen en koppelingsconstanten te correleren met de molekulaire strukturen. Een aantal referentieverbindingen werd bereid door zure dehydratatie van fenchol en borneol. De strukturen van de hierbij ontstane fenchenen zijn reeds eerder onderzocht met behulp van chemische methoden en infrarood spectrometrie. De resultaten van het in dit proefschrift beschreven NMR onderzoek zijn in volledige overeenstemming met de al bekende gegevens. Aan de hand van de strukturen van de etheen-additie produkten konden de strukturen van eerder genoemde tri-methyl-cyclopentadiënen nogmaals worden bevestigd.

REFERENCES

1. R. Huisgen; Angew. Chem. 75, 742 (1964).
2. A.J. v. Pelt jr. and J.P. Wibaut; Rec. trav. chim. 60, 55 (1941).
3. J.P. Wibaut and A.J. v. Pelt jr; Rec. trav. chim. 57, 1055 (1938).
4. W.J. Bailey and J. Rosenberg; J. Am. Chem. Soc. 77, 73 (1955).
5. A. Oppenheim and A. Precht; Ber. 9, 325 (1876).
6. F.C. Whitmore and H.S. Rothrock; J. Am. Chem. Soc. 55, 1106 (1933).
7. E.R. Alexander and A. Mudrak; J. Am. Chem. Soc. 72, 1810 (1950).
8. R.A. Benkeser, J.J. Hazdra and M.L. Burrous; J. Am. Chem. Soc. 81, 5374 (1959).
9. J.C. Scheer; Thesis, Amsterdam (1961).
10. C.H. De Puy and R.W. King; Chem. Revs. 60, 431 (1960).
11. C.A.M.G. Cramers; Fortcoming thesis, Eindhoven.
12. F.H.A. Rummens; Thesis, Eindhoven (1963).
13. L. Chugaev; Chem. Ztg. 24, 542 (1900).
14. J. McKenna and J.B. Slinger; J. Chem. Soc. 1958, 2759.
15. C.A. Bunton, K. Khaleeludin and D. Whittaker; Nature 190, 715 (1961).
16. N.J. Toivonen; Makromolek Chem. 18-19, 414 (1956).
17. J.E. Germain and M. Blanchard; Bull. Soc. Chim. France 1960, 473.
18. D.V. Banthorpe: Elimination Reactions; Elsev. Publ. Comp., Amsterdam (1963), p 195.
19. B.C. Roquitte; J. Phys. Chem. 69, 1351 (1965).
20. K. Alder and H.J. Ache; Chem. Ber. 95, 511 (1962).
21. G. Ohloff, J. Seibl and E. 52. Kováts; Ann. 675, 83 (1964).
22. J. Wolinsky, B. Chollar and M.D. Baird; J. Am. Chem. Soc. 84, 2775 (1962).
23. V.A. Mironov, E.B. Sobolev and A.N. Elizarova; Tetrahedron 19, 1939 (1963).

24. W.R. Roth; Tetrahedron Letters 1964, 1009.
25. K. Alder and E. Windemuth; Ann. 543, 43, 63 (1939).
26. O. Damsky; Ber. 20, 2966 (1887).
27. R. Riemschneider, A. Reisch and H. Horak; Mh. Chemie 91, 805 (1960).
28. R. Riemschneider; Mh. Chemie 91, 809 (1960).
29. R. Riemschneider and R. Nerin; Mh. Chemie 91, 829 (1960).
30. S. McLean and P. Haynes; Tetrahedron Letters 1964, 2385.
31. E.L. Mackor and C. Mclean; Pure and Appl. Chem. 8, 393 (1964).
32. W. von E. Doering and M. Saunders; Tetrahedron 4, 178 (1958).
33. A.P. Ter Borg and H. Kloosterziel; Rec. trav. Chim. 84, 241 (1965).
34. a) W.R. Roth; Angew. Chemie 75, 921 (1963).
b) W. von E. Doering and P. Gaspar; J. Am. Chem. Soc. 85, 3043 (1963).
35. O.L. Chapman and S.L. Smith; J. Org. Chem. 27, 2991 (1963).
36. R.B. Woodward and R. Hoffmann; J. Am. Chem. Soc. 87, 2511 (1965).
37. J.A. Berson and M.R. Willcott; J. Am. Chem. Soc. 87, 2751, 2752 (1965).
38. C. Sandorty, Electronic Spectra and Quantum Chemistry
39. K. Alder and M. Muders; Chem. Ber. 91, 1083 (1958).
40. A. Auterinen; Suomen Kemistilehti 27B, 29 (1954).
41. I.N. Nazarov and A.N. Elizarova; Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk 1951, 295.
42. S.M. Csicsery; J. Org. Chem. 25, 518 (1960).
43. L.J. Bellamy: The IR Spectra of Complex Molecules; Methuen and Co., London (1959), a) p34 b) p13 c)p40 d) p37.
44. D.W. Davies Mol. Phys. 6, 489 (1963), Prentice-Hall Inc (New Yersey); P 341.
45. R. Freeman; Mol. Phys 3, 435 (1960)
46. R. Freeman and Anderson; J. Chem. Phys. 37, 85 (19).
47. O. Diels and K. Alder; Ann. 460, 98 (1927).

48. J.L. Simonsen: The Terpenes, vol II, Cambridge Univ. Press (1957).
49. E.I. Snyder and B. Franzus; J. Am. Chem. Soc. 86, 1166 (1964).
50. P. Laszlo and P. van Ragué Schleyer, J. Am. Chem.Soc. 86, 1171 (1964).
51. F.S. Mortimer; J. Mol . Spectry 3, 528 (1959).
52. F.A.L. Anet; Canad. J. Chem. 39, 789 (1961).
53. T.J. Flautt and W.F. Erman; J. Am. Chem. Soc. 85,3212 (1963).
54. R.R. Fraser; Canad. J. Chem. 40, 78 (1962).
55. J. Meinwald; J. Am. Chem. Soc. 85, 2513, 2514 (1963).
56. N.J. Toivonen; Suomen Kem. A9, 72; B9, 15 (1936).
57. G. Komppa and G.A. Nyman; a) Ann 535, 252 (1938)
b) Ann 543, 111 (1940)
58. E. Pulkkinen; Ann. Acad. Sci. Fennicae AII, 74 (1956).
59. H. Hogeveen; J. Chem. Soc. 1964, 682.
60. L.M. Jackman: Applications of NMR in Organic Chemistry, Perg. Press (1962), P 129.
61. K. Tori; Canad. J. Chem. 42, 926 (1964).

LEVENSBERICHT

Op aanbeveling van de Senaat volgt hier een kort levensbericht van de schrijver.
Hij werd geboren te Heerlen op 12 oktober 1939. Na de lagere school bezocht hij het Grotius College te Heerlen,het eindexamen H.B.S.-B werd afgelegd in 1957.
Aansluitend studeerde hij scheikunde aan de Technische Hogeschool te Eindhoven. Het ingenieursexamen werd afgelegd in januari 1963.
Na beëindiging van de studie trad de schrijver in dienst als wetenschappelijk assistent bij de Groep Instrumentele Aanalyse van de afdeling Scheikundige Technologie van de T.H.E. Onder leiding van de beide promotoren werd gedurende deze periode het onderzoek verricht, dat tot dit proefschrift heeft geleid. In augustus 1965 volgde de benoeming tot wetenschappelijk medewerker bij de groep Instrumentele Analyse.

STELLINGEN

I

FRITZ en KREITER hebben bij de beschrijving van de snelle isomerisatiereakties van trimethylcyclopentadienylsilanen ten onrechte geen rekening gehouden met de mogelijkheid van een H-verschuivings-mechanisme.

H.P. Fritz en C.G. Kreiter
J. Organomet.Chem. 4, 313 (1965)

II

De door NYQUIST gegeven verklaring voor het verband tussen γ_{OH} en de waarden van $(\sigma_p-\sigma_i) + (\sigma_m-\sigma_i)$ is fysisch niet zinvol.

R.A. Nyquist; Spectrochim.Acta 19, 1655 (1963)

III

Gekonditioneerde thermische ontleding, gekombineerd met gaschromatografie en massaspektrometrie kan een machtig hulpmiddel zijn bij de struktuuropheldering. Dit had door SIMON c.s. wellicht beter kunnen worden gedemonstreerd door thermolyse van hoogmolekulaire verbindingen.

W. Simon, J. Völlmin, P. Kriemler, I. Omura en J. Seibl; 3rd Wilkens Gas Chromatography Symposium, Amsterdam 1965

IV

De dimensionering van de door SCHEER gebruikte pyrolysereaktor is zodanig, dat de invloed van verblijftijdsspreiding op de meetresultaten niet verwaarloosd mag worden.

J.C. Scheer; Proefschrift, Amsterdam (1961)

V

De kwantitatieve bepaling van het alkoholgehalte in bloed ter controle op het gebruik van alkoholhoudende drank kan het beste gaschromatografisch geschieden.

VI

De verschillende effekten, welke het oplosmiddel kan hebben op de te meten stof en de interne standaard in de NMR spektroskopie, komen meestal te weinig tot uiting in de nauwkeurigheid, waarmede gemeten resultaten worden vermeld.

N. Lumbroso, T.K. Wu en W.P. Dailey;
J.Chem.Phys. 67, 2469 (1963)

VII

De door Buckingham c.s. afgeleide molekulaire $\Delta\chi$-waarden kunnen van grote betekenis zijn voor de berekening van magnetische bindingsanisotropieën.

A.D. Buckingham, W.H. Pritchard en D.H. Whiffen;
Chem.Commun. 3, 51 (1965)

VIII

Door de huidige, zeer snelle ontwikkeling van de moderne instrumentele analysemethoden bestaat het gevaar dat de organisch-chemici niet steeds zich geheel bewust zijn van de mogelijkheden en limiteringen van de bestaande technieken. Anderzijds hebben de instrumenteel-analytici slechts beperkte gelegenheid, zich volledig te verdiepen in de organisch-chemische problemen.

IX

Door de invoering van de weekend- en avonddiensten is de verhouding arts-patient nadelig beïnvloed. Misschien zou de invoering van de zogenaamde groepspraktijken hierin weer enige verbetering brengen.

Eindhoven, 31 mei 1966 J.W. de Haan