A study in monoterpene chemistry by physical methods

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A STUDY IN MONOTERPENE CHEMISTRY
BY PHYSICAL METHODS

(MET SAMENVATTING IN HET NEDERLANDS)

PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR
IN DE TECHNISCHE WETENSCHAP AAN DE
TECHNISCHE HOGESCHOOL TE EINDHOVEN
OP GEZAG VAN DE RECTOR MAGNIFICUS
DR. K. POSTHUMUS, HOOGLERAAR IN DE AFDELING
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en
prof. dr. C. Koningsberger
## INTRODUCTION

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INTRODUCTION

Present organic chemistry is still mainly based upon the results obtained by classical analysis. However powerful the newest methods of analysis may be, the findings of the classical chemist had only rarely to be corrected. However, the modern organic chemist must more and more rely on the analytical methods of separation, identification and determination of structure, such as analytical distillation, chromatography and counter-current extraction on the one hand, infrared-, ultra violet-, and more recently nuclear magnetic resonance spectroscopy as well as mass spectrography on the other hand. The complexity and variety of the present analytical techniques demand a new type of chemist, with a large interest in Chemical Physics, to supplement the organic chemist, who will cover the field more in general.

Based on these considerations, the Analytical Group of the Eindhoven Technological University was mainly founded to create this type of chemist.

It was thought that in the field of the chemistry of natural products - and more particular in the field of terpene chemistry - a number of attractive aspects would present themselves to be studied by means of an integrated combination of the methods mentioned above.

There are still many questions connected with the structure (in the broadest sense of the word) of monoterpenes. The aim of this thesis is to give an insight into the kind of problems, which thanks to these methods, may be succesfully attacked.

In this connection the following example may be given: Acyclic monoterpenes have the 2,6-dimethyl-octane skeleton (head-to-tail di-isoprene). It is accepted that the cyclic monoterpenes are derived from these by ring closure. The natural acyclic monoterpenene hydrocarbons have three olefinic double bonds. In theory there are 42 possibilities to locate three double bonds in the 2,6-dimethyl-octane skeleton, including "cis" and "trans" isomers, cumulated double bonds excluded.
Of these 42, nature produces only three, viz: myrcene, cis-ocimene and trans-ocimene while the chemist has added another two, viz: cis and trans allo ocimene, which, however, have not yet been isolated in a substantially pure state. This simple example clearly shows the gaps still existing in this narrow field of chemistry, although it has been subject of extensive studies during the last 75 years.

For a successful approach of suchlike problems, it is to be recommended to try these physical methods out on monoterpenes of known structure. This procedure was followed for a considerable part of the investigations, as described in this thesis.

A further object of this study was to prepare monoterpene hydrocarbons of hitherto unknown structure. The pyrolysis of acetates was chosen as being very suitable for this purpose. Moreover, this reaction was considered to have promising kinetical aspects. For instance, there is no general agreement as to the reaction mechanism itself – in spite of the endeavours of many investigators – which was a challenge the more. An insight in this reaction mechanism will supply valuable details about the structure of reactant and reaction products while at the same time optimum conditions for the preparation of new monoterpene hydrocarbons will be found.
1. Introduction

In the general introduction, it has been mentioned that in the chemistry even of alifatic monoterpane hydrocarbons, there is an abundance of unanswered questions and unsolved problems. For instance, one might conceive no less than 42 trienic alifatic monoterpene hydrocarbons, all having the same isoprenoidal skeleton, differing in the place of the three double bonds and cis-trans positions only (allenic structures not included). The number is over one hundred if the members with 4, 2, 1 and no double bond are included. From these compounds, only two have been studied extensively viz. 2,6-dimethyl-octane (I) and myrcene (II), while a few others, e.g. ocimene (III) and allo-ocimene (IV) have long been regarded as single substances, but have recently been recognized by various authors to consist of two isomers (cis and trans) each; there is however no certainty which is which.
When searching for hitherto unknown members of this class the pyrolysis of acetates was considered as one of the most promising ways of producing new monoterpenic olefins. The reaction can easily be controlled, there are at most six primary products (for tertiary acetates) if not just one (primary acetates); furthermore side reactions hardly occur, so that the main components will not be contaminated; at least if the reaction conditions are chosen such that consecutive reactions are as far as possible suppressed. It was felt therefore that prior to the pyrolysis on a more or less laboratory production scale, a thorough study of the pyrolysis reactions on a micro-scale would provide useful information. Such a study is also attractive from another point of view since the problem of the reaction mechanism of the acetate pyrolysis leaves still many questions unanswered, although it has been the subject of many studies during the last four or five decades. Scheer has recently written an excellent review of all the earlier work, and studied subsequently the pyrolysis of a large variety of acetates. He was the first who introduced gas-liquid chromatography (G.L.C.) as an analytical tool into this field and this greatly improved the precision of the reaction rate measurements, and this has led to an improved picture of the reaction mechanism.

It was felt that a further increase in accuracy could be obtained by employing a reactor, designed in such a manner that accurate temperatures could be maintained over the whole reactor in which also the residence time was well defined, and accurately measurable.

By improving the reactor, it is hoped to serve a twofold purpose; throwing some more light on the reaction mechanism and providing at the same time the necessary information for an optimized running of a reactor on preparative scale.

1-2. Requirements and the subsequent general lay-out of the reactor

The basic lay-out of the reactor was inspired by the following four a priori requirements.

I. Reaction and subsequent analysis of reaction product(s) should require little time. Since the reaction products are volatile this requirement could be complied with, by coupling the reactor directly with a gas-chromatograph.

II. Reaction conditions like temperature, concentration and residence time should be well defined, and easy and precisely to measure, so that a high absolute significance can be attributed to the measured reaction rates.
III. Reactor flexibility should be great; especially regarding temperature-range, average residence time, sample introduction, concentration and way of coupling with the gaschromatograph.

IV. The quantity of material needed should be as small as possible, because some of the substances are difficult to obtain in large quantities, in a sufficiently pure form.

The actual lay-out follows from a closer consideration of a number of alternatives:

a. Coupling reactor-gaschromatograph, either in series or parallel.
   In series connection has the limitation of allowing batch-injections only (see also b). Flow systems of reactor and chromatograph cannot be independently controlled, and would influence the choice of carriergas, since this would be identical for both reactor and chromatograph. So it was decided to employ a parallel system.

b. Sample introduction batchwise or continuous.
   Parallel linking (see a) allows the sample introduction to be continuous, so avoiding unwanted concentration-gradients inside the reactor. An injection point could easily be provided for as well, in case only a very small quantity of sample would be available (see also c and e).

c. Reactor type either static or dynamic and for the latter either an ideal mixer or tubular prop flow.
   Static reactors either involve serious difficulties as to heat-transfer, temperature and concentration-gradients or, in order to make these effects vanishingly small, require very long residence-times (of the order of hours). A dynamic guarantees constant reaction conditions. The decision to use a dynamic type of reactor depends as well upon the considerations under a and b.
   Both ideal mixer and tube would be suitable. An ideal mixer however has always a lower efficiency as compared to a tubular reactor, an argument which is important because of the macro-reactor to be used later. An ideal mixer has furthermore a broad residence-time distribution, which should be measured separately and precisely, as otherwise the absolute accuracy of the calculated reaction rates would become much lower as with a comparable tubular reactor.
   In order to avoid this, it was decided to design a tubular reactor (see however also d).

d. In some way or another the sample must be heated up at the entrance of the reactor to reaction temperature from an at least 20°C lower temperature and subsequently cooled down at the end of the reactor. These two temperature fronts mark in fact the beginning and end of the reactor tube or rather: the steeper these fronts are, the better the accur-
acy to which the effective length of the reactor (and accordingly the residence-time) will be known.

Gas-gas heat transfer (by injecting a “cold” sample into a “hot” carrier gas stream at the beginning of the reactor and injecting this mixture into another “cold” carrier gas stream at the end) would certainly allow to construct very steep temperature fronts, but is inattractive because of the complex construction involved.

Heat transfer from the reactor wall in general is inattractive as well, since when the heat transfer towards the centre is stimulated for instance by filling the tube with metal shavings, this would broaden the residence time distribution in an unpredictable way by multipath effects. However, it will be shown here that the requirements could be met with by choosing an open hole tube of proper dimensions.

Consider a gas temperature $T_0$ which will be heated up by passing it through an open hole tube of constant temperature $T$.

The time needed for arriving at the new temperature equilibrium will be equal, in a first approximation, to the time it takes a molecule to travel over an average distance of half the tube diameter $d$. If this time $t$ is to be vanishingly small with respect to the residence time $r$, we have the condition

$$2t < r \cdot 10^{-3}$$

(1)

On the other hand $t$ is given by the Einstein equation

$$t = \frac{X^2}{2D}$$

(2)

Putting $X$ equal to $d/2$ and $D \sim 0.1 \text{ cm}^2 \text{ sec}^{-1}$ (approximate value for molecules of molecular weight of 200 in nitrogen at 500° absolute), and combining (1) and (2) we find the condition

$$d < \frac{1}{50} \cdot \sqrt{r}$$

(3)

meaning that for a chosen residence time of say 25 sec. a tube diameter of 1 mm will overcome the heat transfer problem.

e. Way of residence time measurement, either calculating it from flow, temperature and pressure or by direct measurement.

When we measure gas flow at the outlet of the reactor, and if temperature, average pressure, pressure-drop and volume of the reactor are known, the residence time can be calculated.

With such an arrangement an overall accuracy in residence time of 1% or better is quite difficult to achieve.
It was therefore decided to measure the residence time directly, by mounting thermistors at entrance and exit of the reactor, both thermistors being connected in a D.C. bridge. After injection of a substance in the continuous gas stream, the time between the two out-of-balance pulses can be measured with an electrical chronometer. The general lay-out as determined by the preceding considerations has been depicted in figure 1-1. Figure I-2 shows a photograph of the actual set-up.

1.3. Dimensions of the reactor in connection with residence time and residence-time distribution. Apparent and actual reaction rate.

When there is a laminar flow through a pipe, all molecules will have their own travelling-paths and their residence times will not be equal even when the macroscopic flow is constant in place and time. Such a distribution of residence times, caused by molecular diffusion, reactor type, streamline profiles, concentration-, temperature- and pressure-gradients, can be described as a variation (σ) around an average value (μ).

It must be our first task to estimate the error made in the calculation of reaction rates when one just uses the average residence time instead of taking into account its distribution.

Let us consider a first order reaction, then the conversion factor \(1 - f\) for the \(n_1\) molecules with residence time \(t_1\) will be:

\[
1 - f = 1 - \frac{C_t}{C_0} = 1 - \exp(-kt_1)
\]  

(4)

\(C_t =\) concentration at time \(t\)

\(C_0 =\) starting concentration

\(k =\) reaction rate

Any other residence time will consequently have another conversion factor. One might be tempted to put that

\[
1 - \bar{f} = 1 - \exp(-k't)
\]  

(5)

leading to an apparent reaction rate
Fig. I-2. Photograph of the actual set-up
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\[ k' = \frac{-\ln f}{\bar{t}} \quad \text{or} \quad \bar{t} = \frac{-\ln \bar{f}}{k'} \]  \hspace{1cm} (6)

It will be clear that an error is introduced, at least mathematically, and we must consider how far this apparent reaction rate may deviate from the correct value which follows from

\[ 1 - f = \int [1 - \exp(-kt)] \cdot n_t \, dt \]  \hspace{1cm} (7)

In this expression \( n_t \) is a statistical weight, giving the relative amount of molecules with residence times between \( t \) and \( t + dt \). The distribution function \( n_t \) has to be known in order to solve the integral (7).

We now assume a Gaussian distribution defined by

\[ n_t = \frac{1}{\sigma \sqrt{2\pi}} \exp \left( -\frac{(\bar{t} - t)^2}{2 \sigma^2} \right) \]  \hspace{1cm} (8)

in which \( \sigma \), the variance, is defined as half peak width at the inflection point (is equal to "standard deviation"). Substitution and some straightforward calculations then give the following result:

\[ \bar{t} = k \sigma^2 - \frac{1}{k} \cdot \ln f \]  \hspace{1cm} (9)

When we combine this with (6), we find the correlation between \( k \) and \( k' \)

\[ k \sigma^2 - \frac{1}{k} \ln f = \frac{-\ln f}{k'} \quad \text{or} \quad k = k' \left(1 - k^2 \sigma^2 / \ln f\right) \]  \hspace{1cm} (10)

If we further assume that the correction term \( k^2 \sigma^2 / \ln f \) is small compared to unity, we may write:

\[ \frac{k^2 \sigma^2}{\ln f} = \frac{(k')^2 \sigma^2}{\ln f} = \frac{\sigma^2}{\bar{t}^2} \ln f, \]  \hspace{1cm} (11)

and after substituting this in (10) we arrive at our final result:
\[ k = k' \left[ 1 - \left( \frac{t}{\tau} \right)^2 \right] \ln f \] \hfill (12)

showing that the real reaction rate is indeed larger than the apparent rate. It will be clear as well that for \( \sigma^2 < \tau^2 / 1000 \), the correction will be completely negligible (\( f \) being never lower than 0.1).

It will now be shown that within the concept of the proposed reactor, it is easy to fulfill this condition.

The actual dimensions of the reactor are:

- Inside diameter 0.1 cm
- Total length 1000 cm
- Residence-time range 10-60 sec. (25 sec. average value)
- Reaction-temperature range 450-675° abs. (550°K average value)
- Conversion factor \( 1 - f \) between 0.3 and 0.6

Successively, errors caused by

a. Axial diffusion
b. Temperature profile
c. Heat transfer from the wall
d. Concentration gradients

will now be estimated

First of all we would like to point out that under these conditions the flow will be strictly laminar.

Using \( \eta = 200 \times 10^{-6} \text{ poise} \) and \( \rho = 6 \times 10^{-4} \text{ g/ml} \), a Reynolds number of 12 is obtained.

Taylor* has shown that for laminar flow the residence-time distribution is centred on a point which moves with the mean speed of the flow and is symmetrical about it in spite of the asymmetry of the flow. The dispersion along the tube is governed by a virtual coefficient of diffusivity which is equal to:

\[ D^* = \frac{d^2 u^2}{48 D} \] \hfill (13)

(u stands for mean linear velocity).

For \( d = 0.1 \text{ cm} \), \( u = 40 \text{ cm/sec} \) and \( D = 0.1 \text{ cm}^2/\text{sec} \) we find \( D^* = 0.8 \text{ cm}^2/\text{sec} \).
We can translate the result into a length variance by means of Einstein's diffusion law:

\[ \sigma^2 = 2 D^* \tau = 40 \text{ cm}^2 \]

so that \( \sigma^2/\mu^2 \) becomes \( 40/10^6 = 0.04 \times 10^{-3} \).

Although this is actually a variance in length, the variance in time is identical to it, because of the proportional relationship between length and time.

Both at entrance and outlet of the reactor a slight turbulence will occur because of the rapid change in density. If we assume that this turbulence will be damped out effectively within 20 diameters, we then may put the relative variance caused by this effect equal to:

\[ 2\sigma^2/\mu^2 = 2 \times 20^2/10,000^2 = 0.008 \times 10^{-3} \]

Next there will be a temperature gradient along the reactor wall, again at entrance and outlet, which have been constructed in such a way, however, (see next section) that at both ends the temperature changes will virtually (to within say 0.2°C from the equilibrium values) take place within 10 cm. The variance from this will again be of a Gaussian shape and will accordingly amount to approximately:

\[ 2\sigma^2/\mu^2 = 2 \times 25^2/1000^2 = 0.013 \times 10^{-3} \]

Apart from the reactor wall temperature gradient an extra variance arises in the gas inside because the molecules need time to pick up the heat from the wall. This time variance \( \sigma_t \) is related to \( d^2/8D \) (see section 1 sub d) so that we find:

\[ 2\sigma^2/\mu^2 = 2d^4/64D^2\tau^2 = 0.0005 \times 10^{-3} \]

As a result of the reaction a concentration gradient will occur across the reaction axis, causing on its turn another diffusion term, although purely axial now.

For a 1st order reaction we have

\[ C_z = C_0 \exp (-kz/\bar{u}) \]
or after differentiation:

\[ \frac{1}{C} \frac{dC}{dz} = -\frac{k}{u} \quad (14) \]

Further \( dN/dt \) (total number of molecules diffusing per unit cross section and unit time) is equal to \(-DdC/dz\), this being equal to \(C.dz/dt\) when \(dz/dt\) stands for stationary diffusion velocity. Combining this we find:

\[ \sigma = \Delta z = \frac{-D}{C} \frac{dC}{dz} \Delta t = \frac{Dkt}{u} \quad (15) \]

In which we have taken the liberty of replacing \( dt \) by average residence time \( r \) which is approximately correct for \( f \) not lower than 0.1 (which is equivalent to a nearly constant gradient).

Using \( k = 0.07 \text{ sec}^{-1} \) as an average, we now find:

\[ \frac{\sigma^2}{\mu^2} = \frac{D^2 k^2 (\Delta t)^2}{\bar{u}^2 L^2} = 2 \times 10^{-11} \]

which is vanishingly small.

Finally we like to mention that pressure drop along the reactor does not cause a variance, and that the concentration of reactant is always kept below 0.1% so that the effect of reaction heat is negligible.

As relative variances are additive we may now look for the total residence-time variance which is seen from the preceding discussion to be \(0.2 \times 10^{-3}\) or less, the correction term in (10) being small enough to be neglected, so that we may use (5) for the calculation of the real reaction rates.

It must be stressed that this is only true by virtue of reactor dimensions and reaction conditions chosen.

Describing residence-time distribution in terms of relative variances is a method which is fully explained in a paper by Klinkenberg and Sjenitzer. This method has been chosen for reasons of clarity, and simplicity in calculation.

Cleland and Wilhelm have given a more rigorous treatment on diffusion and reaction in laminar flow tubes but using their symbolism one easily arrives at the same qualitative results.
1-4. **Description of actual construction of the micro reactor and its auxiliary elements**

In this section the essential components: evaporators, reactor, reactor temperature circuit, residence-time circuit, sample loop and gaschromatograph will be described. Reference is made to figures 1 and 2 of the preceding section.

In the evaporator section a constant carrier-gas flow is produced from a gas-cylinder and controlled by a Negretti and Zambra reduction valve (A) and a precision manometer (P). The carrier-gas (always nitrogen in our experiments) is then passed through two evaporators, one containing the substance to be pyrolised, the other containing a reference substance if needed.

Figure I-3 shows a cross section of such an evaporator, which has been constructed in such a way that we may assume that at the prevailing temperature the vapour is saturated. In order to keep the concentration constant at any wanted value, both evaporators were placed into separate liquid-thermostats (B and C).

![Evaporator Diagram](image-url)

**Fig. I-3. Evaporator**
These thermostats (Colora Ultra Thermostat type KLZ 42-60-2-1900) produce a temperature constancy of ± 0.02°C. The temperature of the second evaporator was always chosen a few degrees higher than the first one. Both temperatures were such that the actual concentrations for both sample and reference never exceeded the 100 p.p.m. level.

All connection tubing (copper 5 x 7 mm) throughout the whole reactor system was thermally insulated, and heated by asbestos/copper wire, in order to prevent condensation. Temperature of the tubing was controlled by Variacs. For those cases that there is only a very small quantity of material available, an injection point (D) has been built in, closed off by a siliconrubber disc. As mentioned before, the reactor consists of a capillary tube (copper or stainless steel 1 x 3 mm) wound around a brass block, the whole unit being suspended in an air thermostat (E) (made by Becker Delft, type 1452 SH) which has, within the range 200-400°C, a temperature constancy of ± 0.03°C in time and place. A little above the thermostat cover, two mantles (F and F') have been mounted on inlet and outlet, through which thermostated water of approximately 60°C is circulated from two thermostats (G) (Haake, West-Germany, type FE). Inside the thermostated mantles, the thermistors (H and H') have been fixed (see also figure I-4), both thermistors forming part of a D.C. Wheatstone bridge, fed from a 10-mA constant-current supply.

![Diagram of reactor in- and outlet construction](image-url)
To avoid any catalytic reactions at the wall, the stainless-steel reactor tube was treated with an Alkaterge T (Preussag, Germany) solution. The reactor volume from inlet coupling to outlet coupling, measured with mercury, amounted to 8.23 ml. If we assume that the reaction begins and ends about halfway thermostat coverplate (which is 2 cm from the couplings at either side) some 0.03 ml must be added to find 8.26 ml as the effective volume.

All residence times have to be corrected, because of the distance of 6 cm between thermistors and couplings. After having taken into account the temperature gradient between thermistors and couplings as well, it was found that all measured residence times have to be decreased with 1.5%.

Across the reactor the pressure drop is measured with a mercury differential manometer (K), \( \Delta p \) being usually between 6 and 8 cm.

A precision manometer (L) measures the reactor outlet pressure, which has to be equal to the inlet pressure of the gas chromatograph, as measured by manometer (X). A needle valve (S) has been incorporated to control the outlet pressure.

A precision resistance thermometer (N) (Heraeus model 6011) measures the reactor temperature within \( \pm 0.2^\circ \text{C} \) by means of a D.C. Wheatstone bridge. The reproducibility of the temperature measurements amounted to about \( \pm 0.05^\circ \text{C} \). A Philips valve voltmeter (type GM 6020) with a maximum sensitivity of 100 \( \mu \text{V} \) f.s.d. was used as bridge-balance indicator.

The injection of the reaction products or – when by-passing the reactor – of the non-reacted starting mixture into the gas chromatograph flow system, is achieved by simply turning a sample loop valve (Q). The contents of the loop (about 1 ml) is then inserted as a plug into the carrier gas flow of the chromatograph (see figure I-5).

![Diagram](image-url)
The gaschromatograph consists of the carrier-gas control (X), a thermostat (Becker Delft, type 1452) with the chromatographic column and flame ionization detector, hydrogen- and air-flow controls (Y and Z) and detector amplifier (modified Philips industrial pH meter) plus automatic recorder (Siemens "Kompensograph").

The chromatograph column normally used was a 2 metre copper tube (6 x 8 mm), filled with gaschrom A coated with 1% w/w Alkaterg-T and 15% w/w Apiezon-L as stationary phase.

A hydrogen flame ionization detector was chosen because of its sensitivity, its very good linearity, and its low specificity for molecules of identical carbon-skeleton.

I-5. Way of calculation of $k$, $E^*$ and $\Delta S^*$ from experimental data; estimate of probable errors

**Calculation of $k$ and $\Delta k/k$**

For a first order reaction we have

$$k = \frac{1}{\tau} \ln f \quad (16)$$

$r$ being measured directly by means of the residence-time circuit, while $f = C_t/C_0$ follows from the chromatographic analysis. According to (16) the error in $k$ will be

$$\frac{\Delta k}{k} = \sqrt{(\frac{\Delta r}{\tau})^2 + (\frac{\Delta f}{\ln f})^2} \quad (17)$$

The accuracy of $r$ is not only determined by the actual measurement

$$\Delta r = 0.04 \text{ sec} \quad \frac{\Delta k}{k} = \frac{\Delta r}{\tau} = \frac{0.04}{25} = 0.0016,$$

but also by the uncertainty as to the length of the reactor. From section I-3 we know that for our reactor this is $(\Delta r/\tau)^2 = 13 \times 10^{-6}$ but this is a systematic error rather than an accidental one.

Each $f$ value will be calculated from two chromatograms, one obtained after by-passing of the reactor (peak-areas $A_0$ and $A_1$ referring to sample and reference) and a second one obtained after a travelling time $\tau$ through the reactor (peak areas $A_r$ and $A_2$).

(Non-equality of $A_r$ and $A_2$ is mainly caused by the sample loop valve).

From these data we calculate:
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\[ f = \frac{A_r A_r}{A_o A'_r} \]  

(18)

Peak areas have been measured with a planimeter which had a constant relative error, at least if the peak area exceeds a certain minimum.

Thus we may put:

\[ \frac{\Delta f}{f} = \sqrt{\left(\frac{\Delta A_r}{A_r}\right)^2 + \left(\frac{\Delta A_o}{A_o}\right)^2 + \left(\frac{\Delta A'_r}{A'_r}\right)^2} - 2 \frac{\Delta A}{A} \]  

(19)

\[ \frac{\Delta f}{f \ln f} = \frac{2\Delta A}{A \ln f} \]  

(20)

For \( f < 0.2 \) (80% conversion) \( A_r \) becomes too small to be measured accurately.

For \( f > 0.6 \), \( \ln f \) becomes too small, causing a large error in \( k \) according to (20).

Consequently, an \( f \) value between 0.3 and 0.5 must be recommended, which combined with a \( \Delta A/A \) value of 0.005, corresponds with \( \Delta f/f \ln f = 0.008 \) to 0.014, or 1% as an average value.

Temperature deviations and fluctuations will also effect \( k \) and its accuracy; \( k \) will be proportional to \( \exp \left(-\frac{E^*}{RT}\right) \), so that

\[ \frac{\Delta k}{k} = \Delta \ln k = \frac{E^*}{RT^2} \Delta T \]  

(21)

For our ester pyrolysis \( E^* \approx 45 \text{ Kcal}, R \approx 2 \text{ cal/degree} \) and \( T \) will be 550° abs. average so that:

\[ \frac{\Delta k}{k} = 40 \frac{\Delta T}{T} \]  

(22)

With a \( \Delta T \) value of 0.04° (see preceding section) we find \( \Delta k/k = \pm 0.003 \).

Of course, the absolute temperature scale is not known to this degree of accuracy, therefore a systematic relative error in \( k \) of approximately 0.6% for every 0.1 abs. temperature scale uncertainty will also have to be reckoned with.
Recapitulating: the accidental error in $k$, as caused by residence-time measurement, peak-area measurement and temperature measurement, will amount to

$$\frac{\Delta k}{k} = \sqrt{\left(\frac{\Delta r}{r}\right)^2 + \left(\frac{\Delta f}{f \ln f}\right)^2 + \left(\frac{\Delta T}{T}\right)^2}$$

(23)

$$= \sqrt{2.5 \times 10^{-6} + 100 \times 10^{-6} + 9 \times 10^{-5}} = 0.01$$

from which can be seen that it is determined by analysis accuracy only. The relative systematic error in $k$ is determined by the fact in how far the reactor length ($0.1\%$) and the absolute temperature scale ($0.0\%$ per $0.1^\circ$ absolute) are defined.

**Calculation of $\Delta S^*$ and $E^*$ from experimental data.**

**Estimate of their probable errors.**

From the theory of absolute reaction rates it follows that:

$$k = \frac{k^* Te}{h} \exp \left(\frac{\Delta S^*}{R}\right) \exp \left(\frac{-E^*}{RT}\right)$$

(24)

or:

$$\ln k = \ln \left(\frac{ek^*}{h}\right) + \ln T + \frac{\Delta S^*}{R} - \frac{E^*}{RT}$$

(25)

$k^*$ is Boltzmann's constant and $h$ is Planck's constant; $e = 2.71$.

We also have the equation

$$rk = - \ln f \text{ or } \ln k = \ln (- \ln f) - \ln r$$

(26)

Combining (25) and (26) we find

$$\ln (- \ln f) - \ln r = \ln k^* e/h + \ln T + \Delta S^*/R + E^*/RT$$

or:

$$\ln \frac{(- \ln f)}{T} = \frac{\ln \tau k^* e}{h} + \frac{\Delta S^*}{R} - \frac{E^*}{RT}$$

(27)
This means that there is a linear relationship between \( \ln (-\ln f)/T \) and \( 1/T \) so that, after \( k \) has been measured at several temperatures, \( \Delta S^* \) and \( E^* \) can be easily calculated.

To simplify the calculation, we now put

\[
y = \ln \left( \frac{-\ln f}{T} \right), \quad x = \frac{1}{T}
\]

so that (27) will get the general form \( y = ax + b \).

The relative error in \( x \) will be much smaller than the relative error in \( y \).

Accordingly, \( a \) and \( b \) will be calculated by a least-squares method, relative to \( y \), by minimizing \( \sum (y - y_i)^2 \). We then find

\[
a = \frac{\sum X_i Y_i}{\sum X_i^2} \quad \text{and} \quad b = \bar{y} - a \bar{x}
\]

in which:

\[
X_i = \bar{x} - x_i, \quad Y_i = \bar{y} - y_i
\]

We now proceed to calculate probable errors; from (29) we find:

\[
\frac{\Delta a}{a} = \frac{\sum X_i^2}{\sum X_i Y_i} \cdot \frac{\sum X_i \Delta Y_i}{\sum X_i^2} = \frac{\sum X_i}{\sum X_i Y_i} \Delta Y_i
\]

in which \( \Delta Y_i \) is considered a constant.

\( \Delta Y_i = \Delta (\bar{y} - y_i) \) can be put equal to the standard deviation in \( y \) (std \( y \)).

So we find the relative error in \( E^* \):

\[
\frac{\Delta E^*}{E^*} = \frac{\Delta a}{a} = \pm \frac{\sum X_i}{\sum X_i Y_i} \sqrt{\frac{\sum(y - y_i)^2}{n}}
\]

Further we can see from (28) that

\[
\Delta (\Delta S^*) = \pm R \Delta b = \pm R \Delta r/r
\]

\[
= \pm R \left\{ \sqrt{\frac{\sum(y - y_i)^2}{n}} + \bar{x} \frac{\sum X_i}{\sum X_i^2} \sqrt{\frac{\sum(y - y_i)^2}{n}} + \frac{\Delta r}{r} \right\}
\]

\[(32)\]
In the temperature range studied, \( \bar{x} \), \( \Sigma X_i / \Sigma X_i^2 \) is much smaller than unity, and \( \Delta r/r \) is vanishingly small compared to std. \( y \). Therefore we may write:

\[
\Delta (\Delta S^*) = \pm R \sqrt{\frac{\Sigma (y - y_i)^2}{n}}
\]  

(33)

Combining (32) and (33) we find

\[
\frac{\Delta E^*}{E^*} = \frac{\Sigma X_i}{\Sigma X_i Y_i} \frac{\Delta (\Delta S^*)}{R}
\]  

(34)

Some relationship like this was to be expected, because an error in direction coefficient always implies an error in ordinate cut-off.
CHAPTER II

ACETATE PYROLYSIS, ITS REACTION MECHANISM; EXPERIMENTAL RESULTS ON THE PYROLYSIS OF ACYCLIC MONOTERPENE ACETATES

II-1. A discussion on the reaction mechanism

Acetate pyrolysis has always been a well-known topic of organic chemistry and has been studied very extensively by scores of research workers. In spite of this (or maybe because of it) there is still no unambiguous answer as to the question of its reaction mechanism. The present situation has been ably reviewed by Scheer and will here be summarized briefly.

The most widely adopted mechanism is the one first suggested by Hurd and Blunck involving a six-membered ringsystem as the activated state.

This means essentially that all the valence bonds have to be concerted to each other in such a way that two bonds (indicated by arrows) will break simultaneously in a homolytic way. This model can explain why as a rule a cis-β-hydrogen atom is eliminated, why the reaction is homogeneous and monomolecular and why usually a negative activation entropy is found, and might explain also why β-deuterated acetates react about twice as slowly as their β-hydrogen analogues. The drawbacks of this theory are the well-known facts such as the trans-β-hydrogen elimination observed for some compounds, the constant olefin mixture composition when instead of acetic acid other acids are used, although this does have a large effect on the overall reaction rate, and finally the β-substituent effect.
The main drawback, however, is its inherent unlikeliness from the quantum statistical point of view as will be explained later on in this section. Mcoll has tried to improve the model by introducing an intimate ion pair $R^+CH_3COO^-$ as the transition state, retaining, however, the six-membered ring structure. Now such a heterolytic cleavage is, at least in the gas phase, extremely unlikely because of the excess energy needed as compared to a homolytic dissociation, (figures being 220 against 80 Kcal/Mole).

One might argue, as Scheer in fact does, that the larger part of this energy difference can be compensated by the Coulomb attraction of the two ions, if one assumes that the two fragments are in very close contact in the activated state. This, however, can be hardly a point at all since it implicates that in the transition state the C-OAc bond would be no longer covalent but ionic. The latter is only possible by electronic transition of the molecule, which in order to dissociate would require the full 220 Kcal/Mole as activation energy, while the observed activation energies are usually 40-50 Kcal/Mole. On this account any proposed $E_1$ or $E_2$ mechanism has to be rejected.

It must be stressed, however, that in liquids the possibility of an $E_1$ or $E_2$ mechanism should not be excluded. Moreover there is much chemical evidence against an ionic mechanism for the gas phase pyrolysis as has been amply reviewed by De Puy.

Although the concept of transition states origins from thermodynamics, any realistic picture of an activated state ought to start from a molecular theory. Now this is hardly possible for most of the reaction types and reaction conditions, except for the uni-molecular thermal reaction in the gas phase, from which type we happen to have chosen the acetate pyrolysis. Consider now a single acetate molecule in an inert atmosphere like nitrogen. When heating up this mixture, the surrounding nitrogen molecules, which have picked up extra kinetic energy at the reactor wall will transfer part of their energy to the acetate molecule, which will use the energy to increase its own translational, vibrational and rotational energy; furthermore infra-red radiation from the reactor wall will increase rotational and vibrational
energy of the molecule. Looking for the vibrational energy of a single acetate molecule only, which energy is the most important for the present purpose, the molecule will jump up and down between many vibrational states, until by a certain coincidence of events, its dissociation level is reached. For a large number of molecules there will be a thermodynamic equilibrium between the populations of any two adjacent energy levels, or what is implicated, between the ground state and the highest excited vibrational state just under the dissociation level. The latter state then is, what is called the activated state, the activation energy being the average energy needed to reach it while the activation entropy is nothing else than the entropy difference between the two states mentioned.

From this picture it will be clear that the reaction mechanism must be of the homolytic (radical) type, as usually the dissociation level belonging to the electronic groundstate lies even below the lowest level of the first excited electronic state, which state then never can be arrived at by heating. Only in exceptional cases like e.g. the carotenes where the electronic levels are very close together (causing electronic absorption bands in the visible part of the spectrum) mixing of electronic and vibration levels may occur. Turning now to the point which step is rate determining, there can be hardly any doubt that this must be the C-OAc cleavage, followed by a very rapid attack of the OAc free radical to the "nearest" hydrogen atom.

Before proceeding a general remark. It is true that in fact the whole molecule will be activated and that we always have to refer to vibrational levels of the whole molecule rather than to one of its bonds in particular. But from infrared absorption spectrometry it is known that in many cases rather constant frequencies are found for certain atomic groups, independent of the nature of the rest of the molecule. This is true, for instance, when a light atom (like hydrogen) is connected to a much heavier atom, and when one atom has a much higher electronegativity than the others to which it is connected (like in C=O and C-O-C groups). Only in those cases the vibrational energy will be located for the greater part in a single bond. This means for the acetate pyrolysis that it is sensible to talk about C-H or C-OAc cleavage as possible rate determining steps as will be done in the forthcoming discussion.

There are several reasons now why C-OAc cleavage is much more likely to be the rate-determining step rather than C-H cleavage. Firstly, all C-H oscillators in the molecule are approximately equal and to a large extent independent of the rest of the molecule and so there is no stringent reason why hydrogen atoms near the acetate group would be more easily eliminated than the others. In fact dehydrogenated esters have never been found among the pyrolysis products. Secondly it is known that the dissociation
energy for a homolytic C-H is much higher than for a C-OAc bond (average bond energies are 99 and 85 Kcal/Mole at 20°C), and the activation energies though far from being identical to dissociation energies, must parallel this trend.

Thirdly there is the isotope effect as cited before. Substitution of hydrogen by deuterium makes the C-H oscillator vibrate at \( \sqrt{2} \) lower frequencies and so in a rough approximation the activation energy should decrease with a \( \sqrt{2} \) factor, if C-H or rather C-D cleavage was to be the rate-determining step. Now this would involve a change in reaction rates as given by

\[
\ln \frac{k_h}{k_d} = \frac{E^*_d - E^*_h}{kT^*} = (\frac{1}{2} \sqrt{2} - 1) \frac{E^*_h}{kT^*} = -0.29 \frac{E^*_h}{kT^*}
\]

from which it is clear that not only the order of magnitude for \( \ln k_h/k_d \) is far from the value experimentally found, but what is more important, the sign is reversed. When C-H cleavage would be rate determining, deuteration would increase the rate instead of decrease! The small isotope effect found (indeed small as \( k_h/k_d = 2 \) at 500°K corresponds with only a tiny activation energy difference), will probably originate from the small changes in the electronic groundstate which always do occur upon isotope exchange.

Assumed that C-OAc cleavage is rate determining, it may be tried now to explain the numerous effects on both overall reaction rate and reaction products. To start with the latter, it is clear from the reaction mechanism proposed, that once the acid radical being formed, it no longer matters from what acid if originated. The attack to some neighbouring proton(s) will be independent of the nature of the acid; in other words the composition of the olefin mixture must be constant, as has been reported by all investigators indeed.

The actual olefin mixture composition is in the given hypothesis only determined by sterical and statistical effects; cis-\( \beta \)-hydrogen elimination being preferred only, because a \( \beta \)-hydrogen atom is closest to the acetate radical.

\( \gamma \) and \( \delta \)-hydrogen atoms are unlikely to be removed because of sterical hindrance. From \( \epsilon \)-hydrogen onwards, however, a close approach towards the acetate group is quite easy to make, only it becomes statistically unlikely because the many rotations around single bonds involved, which have to be in concerted action, in order that such an approach will be effectuated.

The negative activation entropy usually found for acetate pyrolysis has long been considered as the main argument for some bridged structure in the activated state. Scheer, however, found activation-entropies between 0 and +6 e.u., for tertiary acetates (-9 to +1 e.u. for secondary and -14 to
-3 e.u. for primary acetates), so actually this argument no longer holds good. Apparently other effects are involved as well. Probably there exists some sterical hindrance in tertiary acetates between the four substituents on the \( \text{Ca} \) atom, strong enough to prevent certain internal rotations. In the activated state all bond lengths will be larger, and it is just conceivable that this releases the sterical hindrance, so increasing the number of rotational degrees of freedom which leads to an increase of entropy. The negative sign of activation entropy which is found for rather non-branched molecules can be explained at least partially by the complete loss of three vibrational degrees of freedom. In the activated state the two radical fragments have to be considered as independent, at least from the vibrational point of view. Suppose now that the original molecule has \( n \) atoms, then the total number of vibrations will be \( 3n - 6 \). When \( n_1 \) and \( n_2 \) are the number of atoms of the two respective fragments \( (n_1 + n_2 = n) \) we find that the total number of vibrations in the activated state will be \( 3n_1 - 6 + 3n_2 - 6 = 3n - 12 \). A third possible entropy effect, namely the number of \( \beta \)-hydrogen atoms present in the molecule, has been mentioned by Scheer. This effect, however, does not apply to the proposed model since the reaction with a \( \beta \)-hydrogen atom will occur after the activated state has been reached and so it cannot contribute to the activation entropy of the molecule.

Direct evidence for the proposed activation - and reaction - mechanism can only be provided by spectroscopic means. One might imagine, for instance, reaction rate measurements under simultaneous irradiation with suitable infrared frequencies. According to our model such optical pumping would decrease the activation energy and increase the reaction rate in a rather predictable way. Also infrared emission spectra of hot ester vapour would give suitable information as well as the vibrational and rotational fine structure electronic spectra may give under certain favourable circumstances.

A last comment on activation concerns the relative importance of entropy compared with energy on the overall reaction rate. From Scheer’s tables it is seen that \( P^* \) varies between 38 and 48 Kcal/Mole which is equivalent to a reaction rate range of \( \exp (9000/2650) = 10^3 \) or three decades \( (T = 650^\circ K \text{ taken as an average}) \). \( (\Delta S^*) \), however, ranges from +6 to -14 e.u. equivalent to a reaction rate range of \( \exp (20/2) = 10^{4.3} \) or nearly 4½ decades. From this follows that the entropy effect may be the predominating one. This statement in connection with the relationship between entropy changes and sterical hindrances as discussed before, suggests the conclusion that within the proposed model, sterical effects are the ones which predominatingly effect the reaction rates.

For a further discussion of the reaction mechanism see section 3 of this Chapter.
II-2. Kinetical measurements on the pyrolysis of tetrahydrolinalyl acetate and linalyl acetate

The reaction rates of the pyrolysis of two acetates were measured at several temperatures.

The reactor described in Chapter I was used for these measurements. Tetrahydrolinalyl acetate was chosen, because it is a simple, saturated tertiary acetate, a compound which can be compared well with the tertiary acetates studied by Scheer.

Linalyl acetate was chosen among other things, because so far no kinetic measurements on the pyrolysis of tertiary acetates with a \( \beta,\gamma \) C=C double bond have been reported. In Tables II-1 and II-2 the actual measurements data have been collected; in figures II-1 and II-2 the Arrhenius plots are given.

Table II-3 shows the algebraic expressions for the Arrhenius plots, and also the calculated activation quantities as well as their probable errors.

It is seen that the results for tetrahydrolinalyl acetate are well within the range of the expected values. Scheer found for tertiary acetates an \( E^\circ \) between 39 and 44 Kcal/Mole, a \( \Delta S^\circ \) between -0.5 and 6.5 e.u. and a reaction rate at reference temperature \( T = 684^\circ K \) between 4 and 10 sec\(^{-1}\). The figures found for linalyl acetate, however, deviate considerably from these ranges. The \( E^\circ = 10.2 \) Kcal and the \( \Delta S^\circ = -45 \) e.u. are in fact the most extreme values ever found for this type of reaction.

These remarkable results might point to some catalytic reaction superimposed on the thermal decomposition. This, however, is not very likely for the following two reasons:

a. It is hard to understand, why linalyl acetate would have this extra reaction, while its tetrahydrogenated derivate does not show any special effect upon pyrolysis.

b. The 20 reaction rate measurements of linalyl acetate which are shown in figure II-2 were obtained by using a stainless steel capillary reactor tube. Four extra reaction rate determinations were made, for which a copper reactor tube was used. These four points (not shown in figure II-2) coincide well with those obtained with the stainless steel reactor tube. It is felt that this excludes the possibility of any specific catalytic reaction.

For a further discussion of the remarkable behaviour of linalyl acetate one is referred to the next section: "pyrolysis of neryl- and geranyl acetate".
### TABLE II-1
**Kinetical data on the Pyrolysis of Tetrahydrolinalyl Acetate**

<table>
<thead>
<tr>
<th>No.</th>
<th>$10^3/T$ (°C)</th>
<th>Residence time $t$ (sec)</th>
<th>$3 + 10^3 \log k$ (k in sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.640</td>
<td>19.1</td>
<td>0.763</td>
</tr>
<tr>
<td>2</td>
<td>1.790</td>
<td>17.4</td>
<td>0.504</td>
</tr>
<tr>
<td>3</td>
<td>1.790</td>
<td>17.4</td>
<td>0.556</td>
</tr>
<tr>
<td>4</td>
<td>1.791</td>
<td>17.4</td>
<td>1.209</td>
</tr>
<tr>
<td>5</td>
<td>1.748</td>
<td>18.1</td>
<td>1.240</td>
</tr>
<tr>
<td>6</td>
<td>1.745</td>
<td>18.1</td>
<td>1.229</td>
</tr>
<tr>
<td>7</td>
<td>1.739</td>
<td>11.2</td>
<td>1.300</td>
</tr>
<tr>
<td>8</td>
<td>1.730</td>
<td>14.8</td>
<td>1.367</td>
</tr>
<tr>
<td>9</td>
<td>1.729</td>
<td>20.0</td>
<td>1.420</td>
</tr>
<tr>
<td>10</td>
<td>1.737</td>
<td>12.2</td>
<td>1.504</td>
</tr>
<tr>
<td>11</td>
<td>1.737</td>
<td>27.2</td>
<td>1.609</td>
</tr>
<tr>
<td>12</td>
<td>1.726</td>
<td>17.9</td>
<td>1.501</td>
</tr>
<tr>
<td>13</td>
<td>1.715</td>
<td>16.8</td>
<td>1.608</td>
</tr>
<tr>
<td>14</td>
<td>1.715</td>
<td>8.7</td>
<td>1.616</td>
</tr>
</tbody>
</table>

### FIGURE II-1
**Arrhenius plot for Tetrahydrolinalyl Acetate**
### Table II-2
Kinetical Data on the Pyrolysis of Linalyl Acetate

<table>
<thead>
<tr>
<th>No.</th>
<th>$10^3/T$ (°C)</th>
<th>Residence time $T$ (sec)</th>
<th>$2 \times 10^3 \log k$ &amp; $\Phi$ in sec$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.137</td>
<td>19.8</td>
<td>0.705</td>
</tr>
<tr>
<td>2</td>
<td>2.137</td>
<td>14.8</td>
<td>0.666</td>
</tr>
<tr>
<td>3</td>
<td>2.132</td>
<td>12.3</td>
<td>0.686</td>
</tr>
<tr>
<td>4</td>
<td>2.132</td>
<td>4.20</td>
<td>0.713</td>
</tr>
<tr>
<td>5</td>
<td>2.119</td>
<td>10.7</td>
<td>0.723</td>
</tr>
<tr>
<td>6</td>
<td>2.119</td>
<td>9.2</td>
<td>0.783</td>
</tr>
<tr>
<td>7</td>
<td>2.100</td>
<td>26.8</td>
<td>0.713</td>
</tr>
<tr>
<td>8</td>
<td>2.100</td>
<td>18.1</td>
<td>0.783</td>
</tr>
<tr>
<td>9</td>
<td>2.087</td>
<td>14.3</td>
<td>0.830</td>
</tr>
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<td>2.087</td>
<td>8.1</td>
<td>0.768</td>
</tr>
<tr>
<td>11</td>
<td>2.076</td>
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<td>9.1</td>
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<td>0.854</td>
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<td>2.061</td>
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<td>0.849</td>
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</tr>
<tr>
<td>18</td>
<td>2.050</td>
<td>4.4</td>
<td>0.864</td>
</tr>
<tr>
<td>19</td>
<td>2.050</td>
<td>8.4</td>
<td>0.853</td>
</tr>
<tr>
<td>20</td>
<td>2.035</td>
<td>7.2</td>
<td>0.895</td>
</tr>
</tbody>
</table>

#### Figure II-2
Arrhenius Plot for Linalyl Acetate
TABLE II-3

<table>
<thead>
<tr>
<th></th>
<th>Tetrahydrocinnamyl acetate</th>
<th>Linalyl acetate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activation equation</td>
<td>$\log k = -8.913/T + 13.04$</td>
<td>$\log k = -2.236/T + 3.470$</td>
</tr>
<tr>
<td>Activation energy $E^*$</td>
<td>$40.6 \pm 1.1$</td>
<td>$19.2 \pm 5.0$</td>
</tr>
<tr>
<td>Activation entropy $\Delta S^*$</td>
<td>$1.0 \pm 1.0$</td>
<td>$-45.0 \pm 4.2$</td>
</tr>
<tr>
<td>St. dev in log $k$</td>
<td>$\pm 0.8 \times 10^{-2}$</td>
<td>$\pm 2.0 \times 10^{-2}$</td>
</tr>
<tr>
<td>St. dev in $k$</td>
<td>$\pm 2.4 \times 10^{-2}$</td>
<td>$\pm 3.4 \times 10^{-2}$</td>
</tr>
<tr>
<td>$k$ (sec$^{-1}$) at reference temperature $T = 684^\circ K$</td>
<td>7.45 sec$^{-1}$</td>
<td>1.59 sec$^{-1}$</td>
</tr>
</tbody>
</table>

II-3. Reaction products of the pyrolysis of a number of monoterpene acetates

In this section the products, obtained from the pyrolysis of seven terpene acetates, are discussed. The pyrolysis experiments were carried out in the macro-scale pyrolysis reactor (see Chapter III for a description). In this way, larger quantities of acetates (up to 250 ml) can be pyrolysed in a relatively short time (up to 24 hrs).

The disadvantage, however, is that no reaction rates can be measured. Furthermore, the macro reactor has a large radial temperature gradient, so that unwanted secondary, tertiary and side-reactions may occur at the hot spots. Bimolecular reactions were hoped to be suppressed by diluting the ester vapour with $N_2$ (1:100). The reaction products were analysed by GLC. As a rule no chromatograms will be given; the reaction products of interest will be characterized by their retention indices. Whenever possible, the products were identified, mainly by comparing their retention indices with those of Table III-2.

The relative quantities in which the compounds were found will be indicated by the following code:

- Relative quantities of 30 - 100% ++++
- Relative quantities of 10 - 30% +++
- Relative quantities of 3 - 10% ++
- Relative quantities of 1 - 3% +

Linalyl acetate

$$(\text{CH}_3)_2\text{C}=\text{CH}_2-\text{CH}_2-\text{C}(\text{CH}_3)(\text{OCOCH}_3)-\text{CH}=\text{CH}_2$$

Pyrolysis temperature 190°C, residence time about 150 sec, conversion about 90%, acetate purity 99.0%. 
As could be expected, the primary products: myrcene and the two ocimenes formed the main components. Supposedly, the allo ocimenes are formed by a secondary reaction, namely by isomerisation of the ocimenes. The presence of limonene and terpinolene is interesting. Most probably they have to be regarded as primary products as well, being formed directly from the monoradical activated state. The presence of neryl- and geranyl acetate is very surprising, the more so as one can be certain that they were not present in the starting material. In the paragraph concerning the pyrolysis of neryl- and geranyl acetate this question will again be dealt with.

**Dihydrolinalyl acetate**

\[
(CH_3)_2 C=CH-CH_2-CH_2-C(CH_3)(OCOCH_3)CH_2-CH_3
\]

Pyrolysis temperature 210°C, residence time about 150 sec, conversion 99%, acetate purity 98.9%.

None of these reaction products could be identified with certainty. Infrared investigation of the reaction mixture gave indications that the main component has the 2-methyl-6-methylene-octene-2 structure. Other products to be expected might be 3,7-dimethyl-2,6-octadiene (cis and trans) and 3,7-dimethyl-3,6-octadiene (cis and trans). On the GLC columns, however, a good separations could not be achieved. Other stationary phases should be tried, both for analytical and preparative-scale columns, before this problem can be solved.
**Tetrahydrolinalyl acetate**

\[(\text{CH}_3)_2\text{-CH-(CH}_2\text{)}_3\text{-C(CH}_3\text{)}(\text{OCOCH}_3\text{-CH}_2\text{-CH}_3\text{)}\]

Pyrolysis temperature 210°C, residence time about 150 sec, conversion 99%, acetate purity 99.9%.

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>Abundancy</th>
<th>10^4</th>
<th>PEG 1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixture of (cis and trans)</td>
<td>++++</td>
<td>941</td>
<td>988</td>
</tr>
<tr>
<td>3,7-dimethyl octene-2 (and -3)</td>
<td>++</td>
<td>958</td>
<td>1040 ?</td>
</tr>
<tr>
<td>2-methyl-6-methylene octane</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

As in the case of dihydrolinalyl acetate, no complete separation of the reaction mixture could be obtained. The first large peak consists of at least two overlapping peaks. Infrared spectra of the raw pyrolysis product and a partially purified sample (by preparative scale GLC) indicated the 2-methyl-6-methylene-octane structure for the smaller component.

**Neryl- and Geranyl acetate**

\[(\text{CH}_3\text{)}_2\text{C=CH-CH}_2\text{-CH}_2\text{-C(CH}_3\text{)=CH-CH}_2\text{-OAc}\]

The pyrolysis of this isomeric pair of acetates is of special importance, because in this way a very stringent evidence as to the reaction mechanism could be obtained.

If the six-membered ring ("concerted") mechanism were the correct one, the activated states of neryl- and geranyl acetate will be non-identical (see figure II-3).

**Figure II-3**

Non identical activated states for neryl- and geranyl acetate in the "concerted" mechanism.
CHAPTER II

FIGURE 11-4a
Pyrolysis products of Geranyl acetate (99.6% pure), at T = 350°K

FIGURE 11-4b
Pyrolysis products of Neryl acetate (98.1% pure), at T = 350°K
It was found, however, that the pyrolysis products of neryl- and geranyl acetate are exactly the same both from a quality and a quantity point of view. In figure II-4 chromatograms of the two products are reproduced. Reaction temperature was 350°C, residence time about 130 sec.

Identical reaction products mean essentially that the activated states must be identical. Identical activated states, however, can in our monoradical hypothesis only be accomplished when in some way or another there is free rotation around the $\beta,\gamma$ carbon-carbon bond. Such a situation can be achieved only if the free electrons on the $\beta,\gamma$ bond are anti-bonding.

In figure II-5 the reaction scheme assumed has been sketched.
In this scheme linalyl acetate has also been included. Its mono radical intermediate will be identical, either to that of neryl- or to that of geranyl acetate, in an approximately 50/50 distribution. Thus in this scheme linalyl acetate must have also the same activated state as neryl- and geranyl acetate, and consequently the reaction products of linalyl acetate should be identical to those of neryl- and geranyl acetate.

This comparison, however, is difficult to make, as linalyl acetate has an at least 1000 times larger reaction rate than both neryl- and geranyl acetate.

In the first paragraph of this section the pyrolysis products of linalyl acetate (pyrolysis temperature 190°C!) have been discussed. These products are not at all identical to those of neryl- and geranyl acetate (see figure II-4). The explanation has to be found in the much higher reaction temperature (350°C) for the latter two acetates.

Therefore, linalyl acetate was pyrolysed again, but now at 350°C. The resulting pyrolysogram is shown in figure II-6.

**Figure II-6**

*Pyrolysis products of linalyl acetate 97% purity (T = 350°C)*

It may be observed that linalyl acetate, indeed, shows all the reaction products expected, but the relative quantities differ from those obtained from neryl- or geranyl acetate. The explanation is that under the given conditions neryl- and geranyl acetate have a conversion of 95-99%, while for linalyl acetate the conversion is probably near 99.999%. Hence, the
average residence times of the primary reaction products of linalyl acetate will be almost twice as long as those of the primary products of neryl- and geranyl acetate. Consequently, the linalyl acetate will show the primary products in lower quantities, and the secondary (and tertiary) reaction products in higher quantities as compared to neryl- and geranyl acetate.

With this complication in mind, convincing evidence about the identity of the activated states of linalyl-, neryl- and geranyl acetate follows from the comparison of figures II-4 and II-6. But there is more evidence. As mentioned before, neryl- and geranyl acetate were found among the pyrolysis products of linalyl acetate. This conclusion was mainly based on an interpretation of the retention indices. Confirmation of this conclusion was supplied by a study of the infrared spectrum of the pyrolysis product. By a combination of GLC and IR it was shown that the reaction product contains about 10% neryl acetate and 15% geranyl acetate.

Figure II-5 shows that this phenomenon is in complete agreement with the proposed reaction scheme. It should be borne in mind that at the linalyl pyrolysis temperature (190°C), neryl- and geranyl acetate are thermally stable!

Finally it may be put forward that the low activation energy (10.2 kcal/mole) and the strongly negative activation entropy (−45 e.u.) found for linalyl acetate, support our anti-bonding activated state theory. Our figures resemble those obtained for the cis-trans isomerisation of butene-2 (E* = 18 kcal/mole and a frequency factor equal to 2 sec⁻¹), a reaction for which also an anti-bonding activated state has been proposed (see Benson S.W. "The Foundations of Chemical Kinetics" Mc Graw Hill Book Company Inc., 1960 page 253-256).

Some suggestions may be made as to further experiments. First of all the measurements of the activation data for the pyrolysis of neryl- and geranyl acetate should be carried out. If our anti-bonding theory is correct, again low activation energies and a low frequency factor will be found. Once the activation data are known, important information about the acetate molecules in the ground state may be obtained. In the ground state the molecule that has the cis structure, will have a higher energy and a lower entropy. Consequently, when two cis-trans isomers like neryl- and geranyl acetate are pyrolysed, the cis structure can be assigned to that isomer which has the smaller E* and the least negative ΔS*.

This kind of structure determination by kinetical measurements can be applied in all those cases where
identical activated states can be expected. As a further example, the two menthol isomers (eee) and (eae) may be mentioned. Most likely their acetates will have identical activated states, while the smaller $E^\circ$ and the least negative $\Delta S^\circ$.

Furthermore, it may be predicted that when neryl acetate is pyrolysed, traces of geranyl acetate will be found among the pyrolysis products and vice versa. This might once more prove the correctness of the proposed reaction scheme.

An analysis of all the peaks of the chromatograms of figure II-4 and II-6 was then undertaken by measuring the retention indices on Apiezon and PEG-4000. A comparison of these indices with those of Table III-2 revealed the probable presence of myrcene, the ocimesnes, the allo ocimesnes, limonene and terpinolene, but no complete analysis could be achieved. Even the two major components could not directly be identified.

**Citronellyl acetate**

Pyrolysis temperature $35^\circ C$, average residence time about 130 sec, conversion $99\%$, acetate purity about $99\%$.

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>Abundancy</th>
<th>$I_{10^5}$</th>
<th>$I_{100}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta^p$-menthene</td>
<td>++</td>
<td>925</td>
<td>1018</td>
</tr>
<tr>
<td>$\Delta^p$-menthene</td>
<td>++</td>
<td>935</td>
<td>1042</td>
</tr>
<tr>
<td>$\Delta^p$-menthene</td>
<td>++++</td>
<td>979</td>
<td>1088</td>
</tr>
<tr>
<td>3,7-diMe-octadiene-1,6?</td>
<td>++</td>
<td>1022</td>
<td>1128</td>
</tr>
</tbody>
</table>

From the reaction product the main component was isolated by prep-scale GLC. Its structure was shown to be that of $\Delta^p$-p-menthene, (see Chapter VI). The presence of $\Delta^3$- and $\Delta^8$-p-menthene as well as of 3,7-diMe-octadiene-1,6 could be proved by an analysis of the IR spectrum of the reaction product. No complete assignment could, however, be made as to which GLC peak is which compound.

**Tetrahydrogeranyl acetate**

Pyrolysis temperature $400^\circ C$, average residence time 120 sec, conversion $>99.5\%$, acetate purity $99.8\%$.

Only one compound (apart from a few traces of other compounds) was obtained. From what is known about the pyrolysis of saturated acetates, 3,7-dimethyl-octene-1 is to be expected as the only reaction product. This
expected structure was indeed confirmed by spectrometrical analysis (see Chapter VI).
The retention indices were found to be:

\[
I_{120}^{Ap} = 901 \quad I_{100}^{PEG} = 942
\]
CHAPTER III

PREPARATION AND PURIFICATION OF SOME MONOTERPENE ALCOHOLS -ACETATES AND -HYDROCARBONS BY DISTILLATION, MACRO-SCALE PYROLYSIS AND MACRO-SCALE GAS-LIQUID CHROMATOGRAPHY

III-1. Description of apparatus

Distillation equipment

Vigreux columns were used for all the distillations. These columns combine a high boil-up and a reasonably good drop of plate and they permit operation under reduced pressures, without too serious a drop of plate-number. Working at reduced pressures (say down to 20 mm) was considered to be quite essential since high boiling temperatures must be avoided. Monoterpene acetates will boil near 250°C, temperatures, at which considerable pyrolysis into acetic acid and olefinic hydrocarbons may occur, especially when secondary or tertiary acetates are involved. In other cases, polymerization was very troublesome at high temperature. The columns were equipped with vacuum mantles (by evacuating at 450°C, a pressure below $10^{-5}$ mm Hg was assured), in which cylindrical aluminium foils were inserted, thus avoiding practically all the unwanted convection- and radiation-heat leakages.

Column diameter was 25 mm, total column length 4 m. A cycle timer with both "open" and "closed" times continuously variable provided a reflux ratio control. Under total reflux at atmospheric pressure the plate number was 30 as measured with heptane-methylcyclohexane.

During each distillation, the bottom temperature, top temperature, total pressure and pressure drop across the column were recorded. Suitable intakes were between 1 and 3 kg, suitable fraction size was 50 g. Usually all the fractions were analyzed by GLC (see next section). Actual conditions and results for each run will be given in section 3 of this Chapter.
Preparative scale gas-liquid chromatograph

This apparatus differed from analytical GLC instruments, mainly as to the dimensions of injection chamber and column diameter. Seven stainless steel columns, each 100 cm long and internal diameter 3.5 cm (except for the tapered ends), were connected to each other with short U tubes (approx. 7 cm long and 0.8 cm internal diameter), so forming an effective column length of 7 m.1) The injection piece had an evaporating chamber 15 cm long and 12 mm internal diameter, filled with copper shavings. In order to promote the sample evaporation, the injection piece had an extra heating wire wound around it. The columns, together with the injection piece, were placed in an air thermostat (Becker, Delft, type 1358-K). The column effluent was led through open hole tubing into a collector. Part of the effluent (usually 2 to 5%) was split off into a hydrogen-flame ionisation detector, the signal of which was measured and recorded in the same way as described in Chapter I.

The effluent tubing also had an extra heating wire wound around it, to prevent any untimely condensation. Temperatures could be measured at injection point, column thermostat and at the effluent tube.

The injection piece and all the connecting tubing was made of copper, while the stainless steel columns were internally coated with an Alkaterg-T film of about 20 Å thickness.

Many experiments were carried out to test the support material on its inertness against olefinic substances. Well known inert support materials such as "Gaschrom - S" and "Embacel" are even not inert enough, and furthermore these materials are much too expensive, seen the large quantities required. The best results were obtained with Sil-O-Cel firebrick of 40-50 mesh. After sintering for 48 hours on 1000°C the support was treated with dimethyl-dichloro-silane (DMDCS) vapour at room temperature. The latter treatment will remove any hydroxyl group from the surface of the support which might be left after the sintering.

After the excess DMDCS has been stripped off, the support is ready to be coated. Silicone oil (General Electric Company) 20% w/w was used as the stationary phase. This rather meagre coating keeps the total residence time relatively short (two to four hours), being an advantage in case of any thermal decomposition reactions of the compounds to be separated. All 1 m segments were tested before being joined together. After that, the whole 7 metres

---

1) According to information kindly provided by the Shell Laboratories, Amsterdam.
column was tested. The following figures will give some indication as to its performance; optimum gas velocity about 1 cm/sec., plate number 2500 and 1100 for 0.1 viz 1.5 ml n-pentane at room temperature. The collector was of a very simple design. A short glass tube of about 12 cm length and 5 mm internal diameter can be connected to the flow output of the chromatograph by means of a ball-joint. This glass tube is fitted into a second glass tube of 15 cm length and 5 cm diameter. The lower 5 cm of the latter tube has a much narrowed internal diameter viz. 3 to 5 mm. Condensation will already start in the first tube, and small drops will fall into the capillary end of the outer tube. The remainder will condense on to the walls of this outer tube (here the linear gas velocity is far below 1 cm/sec) and will, at least partly, run into the capillary as well. Cooling or heating of the collector was usually not required for the work here described. Overall efficiency of the collecting system is over 90%, but only 40% of it will be found in the capillary (this refers to 500 µl of substance to be collected).

**Macro-scale pyrolysis apparatus**

The reactor is essentially a quartzglass tube 110 cm long and 5 cm internal diameter. Two ovens, controlled by two independent thermocouple temperature-regulators heat the sample to any preset temperature. The sample to be pyrolysed is introduced into a preheated nitrogen flow by means of an LKB "Miniflow" micropump. Nitrogen temperature and flow, as well as sample supply, are chosen in such a way as to give rapid evaporation without premature decomposition. The normal capacity is in the order of 15 ml liquid sample per hour. Sample concentration in nitrogen was always somewhat less than 1%. Residence time and reactor temperature were chosen to give a 95-99% conversion. The material collected was washed several times with an aqueous sodium bicarbonate solution, and finally with water. The top layer was dried and then redistilled (if desirable) to remove any residual ester. The lay-out of the macro reactor is sketched in figure III-1.

**III.2. Analytical GLC for purity estimate, distillation- and pyrolysis control**

Throughout this investigation much use has been made of the facilities which analytical GLC may provide. All the distillation fractions, for instance, were analyzed by GLC, usually immediately after the collection of each fraction. In this way, the distillation conditions (pressure, reflux-ratio and the fraction size) could be optimized during the distillation run. After the whole run was completed, an estimate of the purity of each
A STUDY IN MONOTERPENE CHEMISTRY BY PHYSICAL METHODS

FIGURE III-1

acetate supply from minipump

oven temperature control

temperature measurement

N₂ (10 ml/min)

pyrolysis ovens (100-200°C)

N₂ preheating oven (200-400°C)

air cooled condenser

water cooled condenser

flow rator

N₂ from cylinder (~0.5 l/min)

collector
fraction was made. After that, fractions of equal or nearly equal purity could easily be combined. These combined fractions — usually three in number plus the rejected material — were then analyzed again.

Of course GLC plays an important role in the selection of the material to be distilled. Most of the compounds in question are of commercial origin, and therefore analyses were made of any available quality of all the compounds of interest.

GLC was also used for an estimate of the conversion-factor for the macro pyrolysis. As this macro reactor is not so well defined, the conditions required for a 95-99% conversion, are not exactly known beforehand. After a good guess had been made as to the reaction conditions, an analysis was made of the first drop of pyrolysis product. From this chromatogram the conversion factor could be estimated, which permitted a calculation of the changes to be made in temperature or flow. If desired, this procedure can be repeated a second or a third time.

In preparative-scale GLC there is another optimizing problem. One wishes to collect the largest absolute amount of material in the shortest possible total time. However, this can hardly ever be combined with a chromatogram with optimized separation. If the compound to be collected is well separated from its satellites in an analytical chromatogram, more material can be obtained by overloading the preparative-scale column until the peak in question becomes partially overlapped by the neighbouring peak(s), and a suitable part of that peak is cut out. Especially for complex mixtures, or if the compound to be collected is only a minor component of the mixture, this "slicing" technique is to be preferred. The point is to find the correct quantity of material to be injected, with the least loss of separating power. This optimizing process is again controlled by analytical GLC; the collected slice is weighed and its purity estimated.

Purity estimate by GLC is straightforward, but sometimes also misleading. First of all, it happens many times that two compounds have nearly-equal retention indices, so that one may overlook the presence of an impurity, which is hidden under the main peak.

Typical examples are; citronellol-nerol and citronellylacetate-nerylacetate on Apiezon columns and citronellol-geranylacetate, linalol-dihydrolinalylacetate, linalylacetate- tetrahydrogeranyl acetate on Polyethyleneglycol columns (see also Table III-2). Analyzing on two columns of differing polarity is an obvious means to avoid such possible mistakes. All our critical analyses are therefore made on both Apiezon and Polyethyleneglycol columns, and in some cases even a third analysis on Squalane or on Glycerol-trioxy-propionitril was made.
Another difficulty sometimes encountered in purity estimate by GLC, is the thermal or catalytic decomposition of the substances in the gas chromatograph. Thermal decomposition was found, for instance, when analyzing tertiary acetates, linalylacetate in particular. In the chromatogram this kind of pyrolysis is quickly recognized as the peaks of the pyrolysis products have a steep front and a very long tail, which extends in fact as far the position of the "mother"-peak. The phenomenon can directly be proved, and abolished at the same time, by lowering the analysis temperature by 20 to 40°C. (to keep the analysis time constant, the gas velocity has to be increased in accordance). Catalytic decompositions differ from pyrolysis, in as far as the former are concentration dependent. As the concentration of the sample is much higher in the injection piece and in the first part of the column as compared to the concentration in the rest of the column, the catalytic decomposition occurs in the front piece of the column mainly. As a consequence, the peaks of the decomposition products may be almost symmetrical, so that they can easily be mistaken for impurities. A change in analysis temperature will nearly always reveal which of the peaks are real impurities of the material injected. Since the sample size is not accurately known, it should be kept in mind that impurities are found only if they are sufficiently volatile; for instance, dimeric and polymeric products will usually not be found. As a rule this is not opportune for distillation fractions, except when the compound to be purified polymerizes very quickly. This happens, for instance, with myrcene, the ocimenes and the allo ocimenes. Another example of a misleading GLC purity estimate is formed by α-pinene. A two months old α-pinene distillation fraction was analyzed at 120°C on a PEG column; no impurities were found. The infrared spectrum, however, clearly showed the presence of hydroxyl, carbonyl and peroxide bands! The phenomena could be explained as follows; α-pinene is easily oxidized by air-oxygen, the peroxide is the primary oxidation product. The peroxide is not found by GLC because it is rather unstable and decomposes into α-pinene at the analysis temperature. The OH and C=O containing oxidation products were not found by the GLC analysis, because they have much longer retention times than α-pinene. Their possible presence was above all overlooked since they were not expected in this narrow distillation fraction.

The purity estimates of Table III-1 are found not by measuring the relative peak-areas, but by using peak heights only. This is permissible because in this investigation the impurities were small, while their retention values were always close to that of the main peak. (When a purity is calculated from measured impurities the accuracy of the latter measurements need not be great).

For the same reasons no correction is made for detector selectivity effects. Also no dimensions are given for the quoted purities of Table III-1. Whether
the percentage is expressed in weight percentage, volume percentage, mole percentage, mole ratio or weight/volume, the answer will yet be the same. For the applications discussed in this section, the following experimental conditions were used.

<table>
<thead>
<tr>
<th>Columns</th>
<th>copper 4 m, 6 mm internal diameter.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detector</td>
<td>katharometer (differential heat-conductivity cell).</td>
</tr>
<tr>
<td>Temperature</td>
<td>as a rule 180°C for alcohols and esters (or 20 to 40°C lower if thermal or catalytic decomposition occurred at 180°C), and 140°C for hydrocarbons.</td>
</tr>
<tr>
<td>Flow</td>
<td>the optimum linear velocity was found to be in the range of 6 to 8 cm/sec. When the separation was not very critical, or when the analysis time became too long, a 2 or 3 times higher velocity was used.</td>
</tr>
<tr>
<td>Support</td>
<td>Gaschrom-S, 100-120 mesh, treated with 0.5% w/v Alkaterg to increase the chemical inertness.</td>
</tr>
<tr>
<td>Stationary Phases</td>
<td>Apiezon-L, Polyethyleneglycol-4000, and - for some special applications - Squalane and Glyceroltrioxypropionitril.</td>
</tr>
<tr>
<td>Quantity injected</td>
<td>1μl or less. This is important, as otherwise the columns will be somewhat overloaded, which would result in peak broadening. Broadening may easily obscure minor impurity peaks close to the main peak! Under these conditions, bridge current and sensitivity of the bridge must have their maximum values, except for the mean peak, for which the sensitivity must be attenuated by a factor of 5. The detectability achieved in this way amounted to 0.1%. In all the purity estimates 0.2% was subtracted from the purity found, thus anticipating any impurities which might be overlooked.</td>
</tr>
</tbody>
</table>

### III.3. Description of the distillation procedure and the products obtained.

The following monoterpenic alcohols and their acetates were obtained by distillation in highly purified form; linalol, dihydrolinalol, tetrahydro-linalol, geraniol, nerol, citronellol and tetrahydrogeraniol. Also some hydrocarbons like limonene, myrcene, α-pinene and β-pinene were purified for several reference purpose.
Linalol

(3,7-dimethyl-1,6-octadien-3-ol)
Origin ABRAC "Linalol Standard", purity approx 98%, four impurities.
Intake 1010 g, pressure 90 mm, reflux ratio 1.5 : 50 sec.
Yield: 253 g of 99.5% purity and 310 g of 99.3% purity.

Linalyl acetate

(3,7-dimethyl-1,6-octadienyl-3-acetate)
Origin Firmenich quality "extra", Purity 99%. Intake 1040 g, pressure 90 mm, reflux ratio 1.5 : 50 sec.
Yield: 210 g of purity 99.8%.

Dihydrolinalol

(3,7-dimethyl-6-octene-3-ol)
Origin I.F.F. (Polak and Schwartz) purity 89%, 8% linalol and three other impurities.
Intake 1800 g, pressure 130 mm, reflux ratios ranging from 1.5 : 50 to 2 : 40 sec.
Yield: 495 g of 99.6% and 315 g of 99.2% purity.

Dihydrolinalyl acetate

(3,7-dimethyl-6-octenyl-3-acetate)
Origin: Own made by esterification of the I.F.F. dihydrolinalol. The alcohol was refluxed with acetic anhydride in a 1 : 6 mole ratio.
Under these circumstances a 99% conversion was obtained within half an hour, thus keeping the unavoidable acetate decomposition as low as possible. Reaction conditions were optimized with the aid of infrared spectral analysis.
Intake 1350 g product which contained 85% acetate(s), less than 1% alcohol(s) and 15% olefinic hydrocarbons.
Pressure 55 mm reflux ratio 1.5 : 20 sec.
Yield: 275 g of 98.5%, containing 1.5% hydrocarbons, probably formed during distillation, 335 g of 97% purity and 335 g of 93% purity.

Tetrahydrolinalol

(3,7-dimethyl-octanol-3)
Origin I.F.F. (Polak and Schwartz) purity 98%. Intake 1400 g, pressure 130 mm, reflux ratio ranging from 1.5 : 60 to 2.5 : 50 sec.
Yield: 808 g 99.7% pure and 454 g 99.0% pure.
Tetrahydrolinalyl acetate

(3,7-dimethyl-octyl-3-acetate)
Made from the alcohol (see preceding item), by mixing it with a sixfold acetic acid anhydride, and refluxing the mixture for 1½ hours, resulting in about 98% acetate.
Intake 1030 g, pressure 60 mm, reflux ratio 2 : 60 sec, 21 fractions.
Yield: 230 g 99.9% pure, 290 g 99.6% pure and about 350 g of 98.4% purity.

Geraniol

(3,7-dimethyl-(trans) 2,6-octadien-1-ol)
Origin ABRAC quality "meranol parex", purity 97%. Intake 1463 g pressure 90 mm, reflux ratio 1.5 : 60 sec, 25 fractions.
Yield: 578 g 98.8% and 410 g 97.6%.

Geranyl acetate

(3,7-dimethyl-(trans) 2,6-octadienyl-1-acetate)
Origin Firmenich purity 51%, containing 32% citronellyl acetate, 5% nerylacetate and 4 other impurities.
Intake 2700 g, pressure 90 mm, reflux ratio 1.5 : 60, 60 fractions.
Yield: 245 g of 99.6% purity and about 1 kg of 81% purity.

Nerol

(3,7-dimethyl-cis 2,6-octadien-1-ol)
Origin ABRAC quality 99-100, actual purity 95%. Intake 996 g pressure 150 mm, reflux ratio 1.75 : 25 sec, 14 fractions.
Yield: 375 g 99.0% and 420 g of 98.7% purity.

Neryl acetate

(3,7-dimethyl-cis 2,3-octadienyl-1-acetate)
Origin: Own made, starting from ABRAC quality 98 (actual purity 93%) nerol, by refluxing it with 1 : 1.2 mole of acetic acid anhydride during half an hour resulting in a better than 99% conversion.
Intake about 2 kg, reflux ratio 3 : 50, pressure 50 mm, 34 fractions.
Yield: 630 g 98.3% and 480 g of about 97% pure material.

Citronellol

(3,7-dimethyl-6-octen-1-ol)
Origin ABRAC (rhodinol), purity 99%.
Intake 1590 g, pressure 200 mm, reflux ratio 1.75 : 25 sec, 29 fractions.
Yield: 336 g of 99.9% purity and 856 g of 99.7% purity.
**Citronellyl acetate**

(3,7-dimethyl-6-octenyl-1-acetate)

Origin: Firmenich quality "extra" purity 97%.

Intake 1000 g, pressure 130 mm, reflux ratio 2 : 35 sec, 27 fractions.

Yield: 400 g of 99.7% purity.

**Tetrahydrogeraniol**

(3,7-dimethyl-octanol-1)

Origin: I.F.F. (Polak and Schwartz), purity 97%.

Intake 2095 g, pressure 160 mm, reflux ratio 1.5 : 60 sec, 38 fractions.

Yield: 810 g of 99.8% purity.

**Tetrahydrogeranyl acetate**

(3,7-dimethyl-octyl-1-acetate)

Origin: Own made by esterification of I.F.F. tetrahydrogeraniol by refluxing it for half an hour with 1 : 1.2 moles of acetic acid anhydride; purity about 93%.

Intake 1190 g, pressure 20 mm, reflux ratio 1.5 : 30 sec, 16 fractions.

Yield: 551 g of 99.8% purity and 435 g of 99.4% purity.

**Myrcene**

(3-methylene, 7-methyl-1,7-octadiene)

Origin: Glidden, quality 85, actual purity 76%.

Intake 2 kg, pressure 15 mm, reflux ratio 2 : 40, 13 fractions.

Yield: 600 g 93% pure material. This product was redistilled.

Intake 600 g, pressure 15 mm, reflux ratio 1.5 : 60 sec, 17 fractions.

Yielding 140 g of an azeotropic mixture containing 96% myrcene.

For further purification see preparative scale GLC. (yielding 0.5 ml 99.8% pure material)

**Limonene**

(1-methyl-4-isopropylene-cyclohexene-1)

Origin: Glidden purity 98%.

Intake 1.4 kg, pressure 150 mm, reflux ratio 2 : 40 sec, 24 fractions.

Yield: 790 g of 99.8% purity.

**α-pinene**

Origin: North-American Turpentine oil (Chemische Fabriek "Naarden").

Intake three batches of 3.3 kg each, atmospheric pressure, reflux ratio 1 : 20, 91 fractions in total. After analysis, fractions were combined to
CHAPTER III

yield 3.2 kg $\alpha$-pinene of about 95% purity and 1.5 kg of 95% pure $\beta$-pinene. 2 kg of the $\alpha$-pinene was redistilled (same conditions) yielding 600 g 99% pure $\alpha$-pinene. The 1% impurity consisted of the peroxide and related oxidation products; 100 g 99.8% pure $\alpha$-pinene was prepared by percolating the 99% quality through a silica gel column.

$\beta$-pinene

Origin see under $\alpha$-pinene. The 1.5 kg 95% pure material was redistilled. Yield approx. 1 kg 99% pure $\beta$-pinene.

In Table III-1 the distillation results have been summarized.

### Table III-1

**DISTILLATION PRODUCTS**

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>BEST MATERIAL OBTAINED</th>
<th>SECOND BEST MATERIAL</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Amount (g)</td>
<td>Purity (%)</td>
</tr>
<tr>
<td>Linalool</td>
<td>235</td>
<td>99.5</td>
</tr>
<tr>
<td>Linalyl acetate</td>
<td>314</td>
<td>99.3</td>
</tr>
<tr>
<td>Dihydroinol</td>
<td>405</td>
<td>99.9</td>
</tr>
<tr>
<td>Dihydrolynnalol</td>
<td>275</td>
<td>98.5</td>
</tr>
<tr>
<td>Tetrahydroinol</td>
<td>808</td>
<td>99.7</td>
</tr>
<tr>
<td>Tetrahydroinylol</td>
<td>230</td>
<td>99.9</td>
</tr>
<tr>
<td>Geraniol</td>
<td>579</td>
<td>98.8</td>
</tr>
<tr>
<td>Geranyl acetate</td>
<td>245</td>
<td>95.6</td>
</tr>
<tr>
<td>Nerol</td>
<td>370</td>
<td>99.0</td>
</tr>
<tr>
<td>Neryl acetate</td>
<td>435</td>
<td>99.3</td>
</tr>
<tr>
<td>Citroenol</td>
<td>334</td>
<td>99.8</td>
</tr>
<tr>
<td>Citronelly acetate</td>
<td>435</td>
<td>99.7</td>
</tr>
<tr>
<td>Tetrahydrogeraniol</td>
<td>810</td>
<td>99.8</td>
</tr>
<tr>
<td>Tetrahydrogeranyl acetate</td>
<td>550</td>
<td>99.5</td>
</tr>
<tr>
<td>Myrcene</td>
<td>140</td>
<td>91</td>
</tr>
<tr>
<td>Limonene</td>
<td>196</td>
<td>99.8</td>
</tr>
<tr>
<td>$\alpha$-pinene</td>
<td>5100</td>
<td>99.0</td>
</tr>
<tr>
<td>$\beta$-pinene</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### III-4. Physical constants of some pure substances

Once having the pure distillation products, it was thought to be of value when some physical constants - apart from the spectra - were measured. Density, refractive index and molecular optical rotation data have been reported frequently in literature. The present measurements are thought to be of special value because purities have been assessed by GLC. Retention indices have also been included; it is felt that they are of rapidly increasing importance for identification by GLC.

Densities were measured in pycnometers with engraved capillary neck. The pycnometers were calibrated with mercury and water. Measurements were
carried out in a transparent liquid-thermostat at 25.0 ± 0.1°C. The reproducibility was found to be ± 0.0001 or better. All the measurements were repeated three times; after that the average of the three values was taken.

Refractive-index measurements were carried out with a Bausch and Lomb precision refractometer (type 33-45-03-01) at 25.0°C. Again the average out of three measurements was taken. The quoted values for \( n^\mathrm{D}_25 \) have an accuracy of approximately ± 0.00003.

Optical rotations have been measured with the electronic ETL-NPL polarimeter (type 143-A). Cell thickness was 1.00 cm. For substances with a very low rotation, the pure liquids were used. When dilutions were necessary, ethyl alcohol (95%) was used as the solvent. The actual measurements were made at 546 mm. The \( [\alpha]^\mathrm{D}_25 \) values have been calculated with the aid of suitable dispersion formula.

Measurements were carried out at an ambient temperature of 21.5 ± 0.5°C.

Retention indices \( I_x \) are defined by

\[
I_x = 100z + \frac{\log R_x - \log R_z}{\log R_z + 2 - \log R_z} \times 200
\]

Here \( R_x \) and \( R_z + 2 \) stand for the netto retention values of \( n \)-paraffins with \( z \) and \( z + 2 \) carbon atoms respectively; \( R_x \) is the netto retention value for the substance \( x \), whose index \( I_x \) is to be measured. The retention indices defined

<table>
<thead>
<tr>
<th>TABLE III-2a</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHYSICAL CONSTANTS OF SOME MONOTERPENES</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Substance</th>
<th>( \delta_4^\mathrm{D} )</th>
<th>( \delta_0^\mathrm{P} )</th>
<th>( [\alpha]^\mathrm{D}_25 )</th>
<th>Concentration</th>
<th>( \delta_4^\mathrm{B} )</th>
<th>( \delta_0^\mathrm{P} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lilalol</td>
<td>0.3624</td>
<td>1.4601</td>
<td>0.85</td>
<td>pure liquid</td>
<td>14 99</td>
<td>10 85</td>
</tr>
<tr>
<td>Dihydrolinalol</td>
<td>0.3597</td>
<td>1.4588</td>
<td>-0.4</td>
<td>-0.25°</td>
<td>14 16</td>
<td>14 16</td>
</tr>
<tr>
<td>Tetrahydrolinalol</td>
<td>0.4074</td>
<td>1.4510</td>
<td>0.11</td>
<td>-0.12</td>
<td>14 18</td>
<td>13 87</td>
</tr>
<tr>
<td>Geraniol</td>
<td>0.3792</td>
<td>1.4734</td>
<td>0.14</td>
<td>-0.12</td>
<td>15 85</td>
<td>15 16</td>
</tr>
<tr>
<td>Nerol</td>
<td>0.3723</td>
<td>1.4763</td>
<td>0.14</td>
<td>-0.12</td>
<td>15 86</td>
<td>14 16</td>
</tr>
<tr>
<td>Citronellol</td>
<td>0.3845</td>
<td>1.4530</td>
<td>+2.0</td>
<td>+2.2°</td>
<td>14 23</td>
<td>14 06</td>
</tr>
<tr>
<td>Tetrahydrolinalol</td>
<td>0.3530</td>
<td>1.4596</td>
<td>+0.6</td>
<td>-0.5°</td>
<td>15 24</td>
<td>15 64</td>
</tr>
<tr>
<td>Linusal acetate</td>
<td>0.4036</td>
<td>1.4486</td>
<td>-8.5</td>
<td>-7.5°</td>
<td>15 43</td>
<td>12 57</td>
</tr>
<tr>
<td>Dihydrolinalyl acetate</td>
<td>0.3944</td>
<td>1.4411</td>
<td>-1.1</td>
<td>-1.5°</td>
<td>14 64</td>
<td>12 01</td>
</tr>
<tr>
<td>Tetrahydrolinalyl acetate</td>
<td>0.3613</td>
<td>1.4228</td>
<td>&lt;0.1°</td>
<td>&lt;0.1°</td>
<td>13 23</td>
<td>12 12</td>
</tr>
<tr>
<td>Geranyl acetate</td>
<td>0.3165</td>
<td>1.4609</td>
<td>-0.4</td>
<td>-0.35°</td>
<td>14 19</td>
<td>12 93</td>
</tr>
<tr>
<td>Neryl acetate</td>
<td>0.3229</td>
<td>1.4591</td>
<td>&lt;0.1°</td>
<td>&lt;0.1°</td>
<td>14 33</td>
<td>12 93</td>
</tr>
<tr>
<td>Citronellyl acetate</td>
<td>0.3807</td>
<td>1.4413</td>
<td>+2.2</td>
<td>2.0°</td>
<td>15 37</td>
<td>12 60</td>
</tr>
<tr>
<td>Tetrahydrolinalyl acetate</td>
<td>0.3606</td>
<td>1.4237</td>
<td>+0.4</td>
<td>+0.3°</td>
<td>15 69</td>
<td>12 90</td>
</tr>
<tr>
<td>( \alpha )-Pinene</td>
<td>0.2956</td>
<td>1.4747</td>
<td>-5.0</td>
<td>-7.6°</td>
<td>2.1% w/v</td>
<td></td>
</tr>
<tr>
<td>( \beta )-Pinene</td>
<td>0.2727</td>
<td>1.4747</td>
<td>-2.2</td>
<td>-18.8°</td>
<td>1.0% w/v</td>
<td></td>
</tr>
<tr>
<td>Limonene</td>
<td>0.3418</td>
<td>1.5032</td>
<td>+125°</td>
<td>+111°</td>
<td>0.7% w/v</td>
<td></td>
</tr>
</tbody>
</table>
in this way no longer depend on pressure, as a relative retention time does; while moreover the temperature coefficient is very small. Of course, the retention indices depend on the liquid phase chosen. Polyethylene glycol (P) and Apiezon (A) were selected for our measurements. Temperature was 180°C for the alcohols and acetates and 120°C for the hydrocarbons. Retention indices are given not only for the 18 pure terpenes but also for a number of hydrocarbon terpenes, which were found in natural essential oils.

In Table III-2 all the measured physical constants have been collected.

Table III-2b
Retention Index of Terpenes

<table>
<thead>
<tr>
<th>Compound</th>
<th>PEG 4000-100°</th>
<th>Apiezon 120°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Myrcene</td>
<td>1165</td>
<td>978</td>
</tr>
<tr>
<td>Octene-X</td>
<td>1236</td>
<td>1034</td>
</tr>
<tr>
<td>Octene-Y</td>
<td>1252</td>
<td>1048</td>
</tr>
<tr>
<td>Trans-4,5-cis-6,7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>All-octene</td>
<td>1370</td>
<td>1142</td>
</tr>
<tr>
<td>Trans-4,5-trans-6,7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>All-octene</td>
<td>1209</td>
<td>1147</td>
</tr>
<tr>
<td>α-Terpine</td>
<td>1191</td>
<td>1035</td>
</tr>
<tr>
<td>α-Phellandrene</td>
<td>1178</td>
<td>1032</td>
</tr>
<tr>
<td>β-Terpine</td>
<td>1201</td>
<td>1083</td>
</tr>
<tr>
<td>β-Phellandrene</td>
<td>1229</td>
<td>1062</td>
</tr>
<tr>
<td>Limonene</td>
<td>1209</td>
<td>1055</td>
</tr>
<tr>
<td>Terpinolene</td>
<td>1249</td>
<td>1111</td>
</tr>
<tr>
<td>α-Pinene</td>
<td>1042</td>
<td>1051</td>
</tr>
<tr>
<td>β-Pinene</td>
<td>1129</td>
<td>1085</td>
</tr>
<tr>
<td>α-Thujene</td>
<td>1040</td>
<td>926</td>
</tr>
<tr>
<td>Sabine</td>
<td>1137</td>
<td>979</td>
</tr>
<tr>
<td>Δ¹-Carene</td>
<td>1165</td>
<td>1001</td>
</tr>
<tr>
<td>Camphene</td>
<td>1089</td>
<td>979</td>
</tr>
<tr>
<td>β-Fenchene</td>
<td>1075</td>
<td>961</td>
</tr>
<tr>
<td>α-Fenchene</td>
<td>1069</td>
<td>975</td>
</tr>
<tr>
<td>Saturene</td>
<td>1012</td>
<td>879</td>
</tr>
<tr>
<td>Tricyclic</td>
<td>1030</td>
<td>943</td>
</tr>
</tbody>
</table>

1) Calculated from the table of relative retention times relative to limonene, given by Kiesewalter and the Heise Report, after having rounded the retention index of limonene, with sense and understanding as the manifold necessities.
CHAPTER IV

VIBRATIONAL, ELECTRONICAL AND NUCLEAR MAGNETIC RESONANCE SPECTRA OF SOME MONOTERPENES.

IV-1. Introduction

The substances to be described here are all of known structure. So, the aim of this Chapter will not be to elucidate the structures but rather to check the existing, and, if possible, to find new correlations between structure and spectrometrical features.

Vibrational, or infrared (I.R.), spectra of the monoterpenes have been published by several authors (see e.g. the API and Sadtler collections of I.R. spectra and the paper by O'Connor and Goldblatt), but they are of no use for the present purpose. Sometimes the spectra are measured with instruments of lower resolving power than the ones used for this investigation. Furthermore, hardly ever purity estimates are given, usually because of the absence of suitable analysis techniques like G.L.C. Moreover, as a rule the substances are measured as pure liquids, which either involves rather inaccurately known cell thicknesses, or the stronger bands go "off-scale", not to speak of solvent effects which are different for every compound as it is dissolved in itself.

Therefore, it was thought that this situation could be improved by using rather dilute solutions (approx 5% w/w). Carbon tetrachloride (for the 4000-900 cm$^{-1}$ region) and Carbon disulfide (for the 900-650 cm$^{-1}$ region) were selected as solvents. All the spectra were run twice; one with a cell thickness such that even the strongest band would show at least 10% transmission, the other one with a 3 to 5 times larger cell thickness, in order to give more details about the somewhat weaker bands. In this way not only better details about the band position are achieved but also the extinction coefficients or absolute intensities become better defined.

Electronical spectra of monoterpenes without conjugated double bonds have not been found in literature. This is mainly due to instrumental difficulties, as the $C = C$ $\pi$-electron system absorbs between 185 and 205 nanometer
(1 nm = 10 Å), a region where lightsource emissivity, quartzglass transmiss-
ion, stray light, oxygen absorption and detector sensitivity become un-
favourable all at once. Having available, however, an instrument (Cary 14)
which can measure very adequately down to 186 nm, it was felt that some
new findings could be expected when measuring in this rather inaccessible
region.

Nuclear Magnetic Resonance, finally, is such a new technique that in spite
of its enormously growing popularity, little has been published in the
terpene field. The NMR spectra to be presented on the one hand will have
to correspond with the accepted structures, and on the other hand contribute
to specific terpene-NMR knowledge. Correlations derived from these spectra
are thought to be of great importance for a possible interpretation of NMR
spectra of unknown terpenes.

Instrumental details will be given in Chapter VII.

**IV-2. The Infrared spectra**

In this section the spectra of eighteen pure monoterpene compounds will be
reproduced, together with tabulated values of frequencies of maximum
absorbance, extinction coefficients, bandwidths and absolute intensities.
All these spectra were made on a Hilger and Watts H 800 spectrophotometer. Some extra data on this instrument concerning accuracy and resol-
v ing power will be given in Chapter VII. All the identifiable frequencies
will be discussed. The more important findings will be summarized at the
end of this section.

**The O-H stretching**

This vibration occurs in the 3200-3700 cm⁻¹ region. When alcohols are
measured as pure liquids, usually only a diffuse band centered near
3350 cm⁻¹ is found, the broadness of the band probably being caused by
many types of hydrogen bonded agglomerates.

In solution, three main regions can usually be distinguished; a sharp band
(of the monomeric alcohol) near 3600 cm⁻¹ and broad bands near 3450
(dimer) and 3350 cm⁻¹ (polymeric association products). These bands can
be used to make a distinction between primary and tertiary alcohols (pro-
bably secondary alcohols as well). From table IV-1 it can seen that the
sharp O-H band for tertiary alcohols is found at somewhat lower frequencies
(3592-3610 cm⁻¹ ) than for primary alcohols (3608-3615 cm⁻¹ ). This corr-
elation, however, is of little value, partly because of the inaccuracy of the
frequency estimate (± 4 cm⁻¹ in our measurements), partly because the
exact position seems to depend upon the concentration. For very dilute
solutions the correlation is probably more strict, as has already been mentioned by Cole and Jeffries*. Better information follows from the broad bands. Table IV-1 and IV-2 show that the tertiary alcohols absorb near 3475 ± 10 cm⁻¹, while the primary alcohols are found to absorb near 3330 ± 10 cm⁻¹. The explanation probably is that for the tertiary alcohols sterical hindrance prevents the formation of polymeric products, so that the 3475 cm⁻¹ band is assigned to dimeric products. For primary alcohols the formation of polymeric structures is far less hindered, resulting in a much stronger hydrogen bonding and thus absorbing at lower frequencies. Our findings are in agreement with similar work done by Friedel*. It must be noted that other authors usually quote somewhat different regions for the different types of alcohols, but this is due to effects arising from concentration, solvent, temperature and the physical state. The correlation may only be used in a comparative way if all the samples are measured under the same conditions.

Another correlation is found when looking at the intensities. If as a rough measure the product \( \epsilon \Delta \nu \) is taken as the intensity, it is seen that the intensity of the primary alcohols is about 2½ times larger than that of the tertiary alcohols (1250 against 500). Both \( \epsilon \) and \( \Delta \nu \) are larger for the primary alcohols. A possible explanation for this phenomenon may be found in the theory given by Tsubomura*.

The C-H stretching region

This region extends from 2800–3100 cm⁻¹. The absorption band is rather broad as a result of the overlap of a number of narrow bands, but usually the frequencies of each of those narrow bands can be estimated and then correlated to the presence of -CH₃, -CH₂, =C-H and =CH₂ groups. Sometimes even more information can be gathered as to possible cyclic structures and to the nature of the neighbouring atoms of these groups. The highest C-H stretch frequencies are found for the structure =CH₂. A frequency between 3075 and 3095 is usually claimed for this group. From the tables IV-1, IV-2 and IV-3 it is seen that for the five substances having this group a medium intensity band is found well within this region.

The =C(R)H stretching is usually found between 3010 and 3040 cm⁻¹, irrespective whether this =CH group belongs to a mono-, symmetrical di-, or tri-substituted ethylene. First of all we should like to put forward that for all the substances investigated, two bands have been found for this type of structure, namely the one near 3030 cm⁻¹ and a second one near 3060 cm⁻¹, the latter having escaped from the attention so far, probably because of its very low intensity (even 2 to 4 times weaker than the 3030 cm⁻¹ band). Both bands are absent in the hydrogenated analogues. It proved to be impossible
to decide whether one or two = CH(R) groups were present, although in at least one instance (geranyl acetate) a slight indication was found for the splitting of the 3030 cm⁻¹ band into two bands about 10 cm⁻¹ apart.

The asymmetrical CH₃ stretching frequency is always found between 2952 and 2972 cm⁻¹ (see Tables IV-1, IV-2 and IV-3), except for α- and β-pinene, where this band is found at 2980 cm⁻¹. This higher frequency reflects the strain of the 4-membered ring to which two CH₃ groups are attached. This may be a valuable diagnostic tool for recognizing methyl substituted cyclobutane rings.

The in-phase vibration of CH₂ group C-H stretching is normally found at 2926 ± 10 cm⁻¹. In fact, all our substances absorb within these limits.

The symmetrical CH₃ and out-phase CH₂ C-H stretchings are to be found at 2872 ± 10 cm⁻¹ and 2853 ± 10 cm⁻¹ so that usually the two peaks overlap especially when NaCl optics are used. Only two exceptions have been found viz. 2834 cm⁻¹ for α-pinene and 2839 cm⁻¹ for limonene. This probably is due to a resonance splitting, which is found to occur when a structure = C-CH₂ is present, so that the two bands mentioned are probably the low-frequency part of such a doublet.

The carbonyl stretching region

The seven acetates studied all show a very strong absorption between 1735 and 1747 cm⁻¹, which is exactly the region to be expected for alifatic saturated acetates. The effect of the β,γ double band on the alcohol part is apparently of no influence on the C=O stretching frequency. Also the extinction coefficients of 550-600 are well within the limits as quoted by Hampton and Newell.

The C=C stretching region

C=C stretchings are found in the 1580-1690 cm⁻¹ region. Within this region several substitution patterns can be recognized both by frequency and extinction coefficient. The R₁R₂C=CHR₃ group usually absorbs at 1670 ± 8 cm⁻¹ with an ε' of approximately 5. Indeed, all our substances which have at least one trisubstituted ethylenic group absorb in the region mentioned. For substances with one hydrocarbon-like R₁R₂C=CHR₃ group the extinction coefficient is found to range from 4 to 6. However, in nerol, geraniol and their acetates, which have two R₁R₂C=CHR₃ groups, the extinction coefficient is not doubled but amounts to 25-35. The conclusion from this apparently is that oxygen substituted to a Cβ atom increases the intensity. So an absorption band near 1670 cm⁻¹ with an extinction coefficient of 20 to 30 may be assigned to a R₁R₂C=CH(CH₂-O) group. When such a group is present, the absence or
presence of one or more "normal" $R_1 R_2 C=CHR_3$ group(s) may be obscured.
Asymmetrical hydrocarbon disubstituted ethylenes $R_1 R_2 C=CH_2$ are found to absorb between 1640 and 1655 cm$^{-1}$ with extinction of 30 ± 10, or somewhat higher (30-60), if one of the alkyl groups is cyclic, or if $R_1$ and $R_2$ form a ring. Our substances limonene and $\beta$-pinene (see Table IV-5) fit well into this picture. Again an extinction coefficient figure is used to differentiate between substitution types.
Vinyl groups $RHC=CH_2$ absorb in the 1635-1650 cm$^{-1}$ region, with extinction coefficients usually between 30 and 50. The frequencies found for linalol and its acetate fit correctly in the region quoted, but the extinction coefficients are somewhat low (see Table IV-1 and IV-2). Literature investigations showed that for a large number of allyl ethers, allyl alcohols and their acetates the $\varepsilon$ varied between 9 and 22, which confirmed our finding.
Mycenel (see Table IV-5) shows, apart from the 1675 band, a doublet at 1635 and 1596 cm$^{-1}$ (extinction coefficients 12 and 73 respectively). This is typical for an asymmetrically substituted conjugated diene with one or two $=CH_2$ endgroups.
has given some numerical data.
As part of our preliminary work we rechecked the figures quoted by these authors and also extended our investigations to some related compounds. In Table IV-6 our own results are compared with those of the authors mentioned.

**Table IV-6**

**Absolute intensities of CH\(_2\) and CH\(_3\) bands between 1330 and 1510 cm\(^{-1}\) (valid only for hydrocarbons)**

<table>
<thead>
<tr>
<th>VIBRATION</th>
<th>FRANCIS(^a)</th>
<th>LUTHER AND CZERWONY(^b)</th>
<th>OWN WORK</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\delta) CH(_2)</td>
<td>A.10(^b)</td>
<td>Integration limits</td>
<td>A.10(^b)</td>
</tr>
<tr>
<td>asymmetrical (\delta) CH(_2)</td>
<td>2.32</td>
<td>2.17</td>
<td>1.7</td>
</tr>
<tr>
<td>symmetrical (\delta) CH(_2)</td>
<td>5.44</td>
<td>6.38</td>
<td>5.2</td>
</tr>
<tr>
<td>(\delta) CH(_3) in 5 or 6 ring</td>
<td>3.94</td>
<td>4.25</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.2</td>
</tr>
</tbody>
</table>

\(a = \frac{1}{2} c / \nu\) for cm\textsuperscript{-1}/mole.

\(\nu = \text{frequency in cm}^{-1}\)

\(c = \text{cm} / \text{mole}\)

For experimental details of the mentioned own work one is referred to Chapter VII. In Table IV-7 the absolute intensities measured for the seven alcohols, their acetates and the four hydrocarbons are given, as well as their intensities calculated from Table IV-6 (sixth column).

From Table IV-7 it is seen that all the measured intensities are much higher than those, calculated from our group-intensities of Table IV-6.

As far as the alcohols are concerned, there are two possible explanations. First of all, the C-OH deformation may absorb in the 1330-1510 cm\(^{-1}\) region. Secondly at least part of the differences can be understood by assuming that a O-CH\(_2\)-C methylene group has a much higher intensity than a hydrocarbon -CH\(_2\) group. In order to check the latter possibility, the \(\delta\)CH\(_2\) intensity of dioxan was measured resulting in a A.10\(^b\) = 3.0 per O-CH\(_2\) group. This is only 1.3 unit more as compared to a hydrocarbon CH\(_2\) group.

In the seventh column of Table IV-7 the differences between measured and calculated intensity in the 1330-1510 cm\(^{-1}\) region have been tabulated. This excess intensity is assigned (after a small correction for the O-CH\(_2\) group) to the C-OH deformation. The absorption band in question is probably rather broad and has its centre somewhere near 1390-1400 cm\(^{-1}\). The intensity of this C-OH deformation so obtained varies from 24.10\(^b\) to 46.10\(^b\) absolute units.

The large discrepancies found for the acetates is probably caused by large
### Table IV-7

**Intensities of CH<sub>2</sub> (1410-1510 cm<sup>-1</sup>), Asymmetrical CH<sub>3</sub> (1410-1510 cm<sup>-1</sup>) and Symmetrical CH<sub>3</sub> (1330-1410 cm<sup>-1</sup>)**

<table>
<thead>
<tr>
<th>Compound</th>
<th>A.10&lt;sup&gt;8&lt;/sup&gt; δCH&lt;sub&gt;2&lt;/sub&gt; and asymmetrical δCH&lt;sub&gt;3&lt;/sub&gt;</th>
<th>A.10&lt;sup&gt;8&lt;/sup&gt; δC=O-H of acetate group</th>
<th>A.10&lt;sup&gt;8&lt;/sup&gt; asymm. δCH&lt;sub&gt;3&lt;/sub&gt;</th>
<th>A.10&lt;sup&gt;8&lt;/sup&gt; symm. δCH&lt;sub&gt;3&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experimentally found</td>
<td>Calculated from Table IV-6</td>
<td>Experimentally found</td>
<td>Calculated from Table IV-6</td>
</tr>
<tr>
<td>Linalol</td>
<td>CH₃-C(CH₃)=CH-(CH₂)₂-C(CH₃)(OH)-CH=CH₂</td>
<td>36.5&lt;sup&gt;1)&lt;/sup&gt;</td>
<td>19.1</td>
<td>29.3</td>
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<tr>
<td>Dihydrolinalol</td>
<td>CH₃-C(CH₃)=CH-(CH₂)₂-C(CH₃)(OH)-CH₂-CH₃</td>
<td>38.0&lt;sup&gt;2)&lt;/sup&gt;</td>
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<td>33.6</td>
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<tr>
<td>Tetrahydrolinalol</td>
<td>CH₃-C(CH₃)=CH-(CH₂)₃-C(CH₃)(OH)-CH₂-CH₃</td>
<td>35.0&lt;sup&gt;3)&lt;/sup&gt;</td>
<td>27.7</td>
<td>32.7</td>
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<td>Geraniol</td>
<td>CH₃-C(CH₃)=CH-(CH₂)₂-C(CH₃)=CH-CH₂-OH</td>
<td>44.4&lt;sup&gt;4)&lt;/sup&gt;</td>
<td>20.8</td>
<td>34.7</td>
</tr>
<tr>
<td>Nerol</td>
<td>CH₃-C(CH₃)=CH-(CH₂)₂-C(CH₃)=CH-CH₂-OH</td>
<td>43.8&lt;sup&gt;4)&lt;/sup&gt;</td>
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<td>32.6</td>
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<td>Citronellol</td>
<td>CH₃-C(CH₃)=CH-(CH₂)₂-C(CH₃)-CH₂-CH₂-OH</td>
<td>35.6&lt;sup&gt;4)&lt;/sup&gt;</td>
<td>22.5</td>
<td>27.5</td>
</tr>
<tr>
<td>Tetrahydrogeraniol</td>
<td>CH₃-C(CH₃)=CH-(CH₂)₃-C(CH₃)-CH₂-CH₂-OH</td>
<td>39.0&lt;sup&gt;4)&lt;/sup&gt;</td>
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<td>21.4</td>
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<tr>
<td>Linallyl acetate</td>
<td>CH₂-C(CH₃)=CH-(CH₂)₂-C(CH₃)(OCOCH₃)-CH=CH₂</td>
<td>50&lt;sup&gt;1)&lt;/sup&gt; &amp;&lt;sup&gt;2)&lt;/sup&gt;</td>
<td>19.1 &amp;&lt;sup&gt;2)&lt;/sup&gt;</td>
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<td>Dihydrolinalyl acetate</td>
<td>CH₂-C(CH₃)=CH-(CH₂)₃-C(CH₃)(OCOCH₃)-CH₂-CH₃</td>
<td>59.3&lt;sup&gt;1)&lt;/sup&gt; &amp;&lt;sup&gt;2)&lt;/sup&gt;</td>
<td>26.0 &amp;&lt;sup&gt;2)&lt;/sup&gt;</td>
<td>64.0</td>
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<tr>
<td>Tetrahydrolinalyl acetate</td>
<td>CH₂-C(CH₃)=CH-(CH₂)₃-C(CH₃)(OCOCH₃)-CH₂-CH₃</td>
<td>56.8&lt;sup&gt;3)&lt;/sup&gt;</td>
<td>27.7&lt;sup&gt;2)&lt;/sup&gt; &amp;&lt;sup&gt;2)&lt;/sup&gt;</td>
<td>61.4</td>
</tr>
<tr>
<td>Geranyl acetate</td>
<td>CH₂-C(CH₃)=CH-(CH₂)₂-C(CH₃)=CH-CH₂-OOCOCH₃</td>
<td>51.7&lt;sup&gt;3)&lt;/sup&gt;</td>
<td>20.8&lt;sup&gt;2)&lt;/sup&gt;</td>
<td>54.2</td>
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<tr>
<td>Neryl acetate</td>
<td>CH₂-C(CH₃)=CH-(CH₂)₂-C(CH₃)-CH₂-OOCOCH₃</td>
<td>54.0&lt;sup&gt;3)&lt;/sup&gt;</td>
<td>20.8&lt;sup&gt;2&lt;/sup&gt;</td>
<td>54.6</td>
</tr>
<tr>
<td>Citronellyl acetate</td>
<td>CH₂-C(CH₃)=CH-(CH₂)₂-CH(CH₃)-CH₂-OOCOCH₃</td>
<td>57.2&lt;sup&gt;3)&lt;/sup&gt;</td>
<td>22.5&lt;sup&gt;2&lt;/sup&gt;</td>
<td>55.5</td>
</tr>
<tr>
<td>Tetrahydrogeranyl acetate</td>
<td>CH₂-C(CH₃)=CH-(CH₂)₂-CH(CH₃)-CH₂-OOCOCH₃</td>
<td>49.4&lt;sup&gt;2)&lt;/sup&gt;</td>
<td>24.3&lt;sup&gt;2&lt;/sup&gt;</td>
<td>51.6</td>
</tr>
</tbody>
</table>

1) after subtraction of =CH₂ absorption near 1415 cm<sup>-1</sup>  
2) acetate -CH₃ absorption not included  
3) without subtraction of =CH₂ absorption
intensities of the acetate CH₃ group. Average intensities of \((29 \pm 4) \times 10^{-8}\) and \((40 \pm 5) \times 10^{-8}\) cm²/molecule/sec may be quoted for the asymmetrical and the symmetrical acetate CH₃ deformations respectively. Some more figures regarding absolute intensity of acetate CH₃ groups could be derived from the spectra of 6 simple saturated acetates. n-Pentyl-acetate, 3-Me-butan-1-acetate, pentanol-2-acetate, 3-Me-pentanol-2-acetate, tert. amyl-acetate and 3-Me-pentanol-3-acetate gave \(A = 25 \times 10^{-8}\) and \(A = 41 \times 10^{-8}\) cm²/molecule/sec as average values for the asymmetrical and symmetrical acetate CH₃ deformations respectively.

These values seem to be restricted to acetates only. Acetone, for instance which has a very similar O=C-CH₃ group has intensities of only 7.5 and 15.0 cm²/molecule/sec per CH₃ group for the two respective absorptions. The figures quoted may serve to identify the presence of C-OH or OCOCH₃ groups, but in fact there are better and easier ways to achieve this. Better agreement with the expected intensities is obtained with the four hydrocarbon terpenes. Only the 1410-1510 cm⁻¹ intensity is 5-10 absolute units too high for \(\beta\)-pinene, limonene and myrcene. This difference can be ascribed to the \(=\text{CH}_2\) in plane deformation; this vibration is not found as a separate band near 1410 cm⁻¹, but is most probably hidden under the \(-\text{CH}_3\) and \(-\text{CH}_2\) absorptions. The presence of a \(=\text{CH}_2\) group may also explain why the 1330-1410 cm⁻¹ intensity is somewhat too high for the compounds just mentioned; the \(=\text{CH}_2\) absorption band will have an intensity contribution below 1410 cm⁻¹.

The C–O stretch and C–O deformation frequencies of alcohols

Alcohols always show two strong bands, one in the 1300-1450 cm⁻¹ region (which is overlapped by CH₂ and CH₃ absorptions, see preceding section) and a second one in the 1000-1150 cm⁻¹ region, the latter being assigned usually to the C–O stretching vibration. For primary alcohols an average value of 1050 cm⁻¹ is quoted, and from Table IV-2 we see that citronellol and tetrahydrogeraniol fit very well, but that nerol and geraniol absorb about 50 cm⁻¹ lower. This is undoubtedly due to the \(\beta\),\(y\) C=C double band. Consequently, the strong absorption near 1000 cm⁻¹ can be used as an indication for the C=C-CH₂OH structure. The same trend is found for the three tertiary alcohols. Dihydrolinalol and tetrahydrolinalol show a complex band (caused by branching at Ca!) centered around 1160 cm⁻¹, which is the expected frequency, while linalol absorbs at a 40 cm⁻¹ lower frequency, indicating the C=C-C(OH)R₁R₂ structure. By this lowering, the frequency falls in the region where the saturated secondary alcohols absorb as well, so some precaution must be
taken when this correlation is used. The extinction coefficients of this C-O stretch seem to be quite independent of substitution, and amount to 45-65.

**The C-O stretching frequencies of acetates**

Quite analogous to alcohols, esters also show two strong bands. The one near 1240 cm⁻¹ (extinction coefficient 400-600) seems to be largely independent of substitution, and is accordingly assigned to the CO-COCH₃ stretching. The second one (probably the C-OCOCH₃ stretching) is found near 1050 cm⁻¹ for primary, and near 1020 cm⁻¹ for tertiary acetates. Like the C-O stretch of the alcohols just discussed, a β,γ C=C double band lowers the frequency about 30 cm⁻¹.

**The RHC=CH₂ out-of-plane deformation**

Two bands near 910 and 990 cm⁻¹ are usually found for vinyl compounds. Substitution of the Cβ atom, especially with C=C groups or -OR groups slightly raises both frequencies. This in fact has been found for linalol and linalylacetate. Especially the rise of the lower frequency up to 922-925 cm⁻¹ may be considered a rather reliable indication that some polar group is attached to the Cβ carbon atom. Usually the low-frequency peak is somewhat stronger (ε' ~100) than the high-frequency peak (ε' ~50).

Myrcene shows both bands as well, although with somewhat increased intensities (ε's equal to 80 and 140).

**The R₁R₂C=CHR₃ out-of-plane deformation**

This band will usually be found at 890 cm⁻¹, and, indeed, limonene and myrcene (see Table IV-5) show the band in the expected region. β-pinene, however, absorbs at 875 cm⁻¹ with an increased intensity (ε' = 170), which is typical for strained ring structures with an exocyclic =CH₂ group. The myrcene band intensity is also markedly high (ε' = 190), but this may be due to the conjugation with the vinyl group, the latter which, as mentioned before, also showed enhanced intensities for the out-of-plane deformation frequencies.

**The R₁R₂C=CHR₃ out-of-plane deformation**

This band is more variable in position and extinction. For noncyclic hydrocarbon-type molecules the absorption will be found between 810 and 840 cm⁻¹ (ε' = 20-40) which corresponds with the results found. If either R₁ and R₂ or R₁ and R₃ from a ring, a decrease in frequency will
be found combined with an enhanced intensity. So cyclohexenic rings with a group $R_1 R_2 C=CHR_3$ will absorb near 800 cm$^{-1}$ (see limonene). A further increase of the strain (such as found in $\alpha$-pinene) may decrease the frequency down to 780 cm$^{-1}$ with considerably enhanced intensities. Oxygen substituted to a C$\beta$atom does not seem to alter either frequency or intensity. Nerol and geraniol have two $R_1 R_2 C=CHR_3$ groups and it is seen that the band intensity, as given, for instance, by the product $\varepsilon$. $\Delta\nu$, is about twice as much as for citronellol, which has only one such a group. The same applies to the corresponding acetates.

The $C=CH_2$ in-plane deformation

Although it is well known that this vibration occurs near 1420 cm$^{-1}$, only linalol, linalylacetate and myrcene show this band, while limonene and $\beta$-pinene do not show a trace of it. Probably the frequency is not as constant as it is thought to be, so that the band may be hidden under the CH$_2$ and CH$_3$ deformation bands near 1450 cm$^{-1}$.

The in-plane deformation of RHC=CH$_2$ groups

Apart from the 1420 cm$^{-1}$ band just mentioned, vinyl groups have a second medium-intensity in-plane deformation near 1300 cm$^{-1}$. Linalol and its acetate both show a strong band at 1414 cm$^{-1}$. The second in-plane vibration could not be identified among the strong general absorption found in that region.

The in-plane deformation of $R_1 R_2 C=CHR_3$ groups

This vibration could in no case be identified because the region 1390-1375 cm$^{-1}$ coincides completely with the symmetrical CH$_3$ deformation region.

Some skeletal deformations

All the acetates studied show a medium intensity band close to 950 cm$^{-1}$. As this band is neither found in the corresponding alcohols nor in the corresponding formates or propionates, it is assumed to be caused by a stretching or deformation of the whole acetate CH$_3$ group, relative to the rest of the skeleton.

If a number of adjacent (CH$_2$) groups are present in the molecule, a typical rocking frequency is found in the 720-725 cm$^{-1}$ region. It is usually assumed that this band will be found if there are at least 4 adjacent CH$_2$ groups. The four saturated compounds studied have only 3 adjacent CH$_2$ groups, and now a weak band between 731 and 735 cm$^{-1}$ is found. The other ten acyclic
terpene alcohols and acetates have only two adjacent \( \text{CH}_2 \) groups and they all absorb between 738 and 744 cm\(^{-1}\). As may be expected, the hydrocarbon terpene compounds show some anomalies; for two adjacent \( \text{CH}_2 \) groups a weak band between 745 and 765 cm\(^{-1}\) has been observed. It is clear, however, that the position of this rocking frequency may provide a useful indication as to the number of adjacent \( \text{CH}_2 \) groups.

Furthermore, we have been looking for isopropyl skeletal frequencies. Bands near 1170, 1140 and 850 cm\(^{-1}\) have been reported for the typical \(-\text{CH(CH}_3)_2\) vibrations. The four saturated terpene compounds clearly show the three frequencies quoted. The ten unsaturated alcohols and esters have a more or less modified isopropyl group or rather an isopropylidene group \( \text{RHC} = \text{C(\text{CH}_3)_2} \).

From Tables IV-1 to IV-5 it can be seen that in all appropriate spectra the \( \nu_4 \) frequency is found between 840 and 880 cm\(^{-1}\), although this weak band is often partly obscured by the much stronger \( \text{R}_1 \text{R}_2 \text{C} = \text{CHR}_3 \) o.o.p. deformation near 830 cm\(^{-1}\). The \( \nu_2 \) and \( \nu_3 \) frequencies seem sometimes to collapse into one frequency between 1170 and 1190 cm\(^{-1}\).

The band or doublet in the 980-1000 cm\(^{-1}\) region assigned by Naves and Lecomte\(^*\) to a vibration of the \( \text{R}_1 (\text{CH}_3) \text{C} = \text{CHR}_2 \) group was not found in any of our spectra. On the other hand, a rather similar doublet (or sometimes a single band) of medium intensity was found in the 1090-1110 cm\(^{-1}\) region for most of our substances carrying a \( \text{R}_1 (\text{CH}_3) \text{C} = \text{CHR}_2 \) group. Linalol is an exception, probably because of the strong alcohol band at 1112 cm\(^{-1}\), and in dihydrolinalyl acetate this band fails as well for no obvious reason. The vibration mentioned may be due to a \( =\text{C-CH}_3 \) stretching or an in-plane \( =\text{C-CH}_3 \) deformation, in analogy to the 950 cm\(^{-1}\) band mentioned, which was assigned to the \( \text{O=\text{C-CH}_3} \) structure.

Finally some ring deformation frequencies might have been found for the three cyclic terpenes studied. The available material, however, proved to be too limited to assign any such band. Only a medium intensity band near 1250 cm\(^{-1}\) may be mentioned, which was found in three spectra, which reminds of the 1260 band quoted by Sheppard\(^*\) for cyclohexane derivatives.

In general, it may be said that the assumed structures are in close agreement with the infrared spectra.

The structures, once being taken to be correct, allowed for the derivation of a number of new or revised correlations, which will be summarized now.

1. The OH stretching of tertiary and primary alcohols will be found (in 1-5% solutions in \( \text{CCl}_4 \)) near 3475 and 3330 cm\(^{-1}\) respectively, the latter having a roughly 2.5 times larger band intensity.
2. The =C-H stretching gives rise to two frequencies, near 3030 and 3060 cm\(^{-1}\), the latter being very weak.

3. CH\(_3\) groups attached to a cyclobutane group absorb near 2980 cm\(^{-1}\).

4. The 1670 cm\(^{-1}\) vibration of R\(_1\)R\(_2\)C=CH(CH\(_2\)O) groups shows an enhanced extinction coefficient of about 25.

5. The 1640 cm\(^{-1}\) C=C stretching frequencies of H\(_2\)C=CH-C(OH)R\(_1\)R\(_2\) derivatives have a much decreased intensity (\(\epsilon\) between 10 and 20).

6. Alcohols absorb between 1330 and 1510 cm\(^{-1}\). The diffuse band - probably the C-OH deformation frequency - has its centre near 1390-1400 cm\(^{-1}\). The absolute intensity is rather variable; values from \((25-46) \times 10^{-8}\) cm\(^2\)/molecule/sec have been found.

7. The acetate CH\(_3\) group has much higher intensities for the asymmetrical and symmetrical deformations than the hydrocarbon-type CH\(_3\) groups. Values of \((29 \pm 4) \times 10^{-3}\), for the 1410-1510 cm\(^{-1}\) region, and \((41 \pm 5) \times 10^{-8}\) cm\(^2\)/molecule/sec for the 1330-1410 cm\(^{-1}\) region are quoted.

8. A \(\beta,\gamma\) C=C double bond shifts the C-O stretching frequency of alcohols and their esters to a 30-60 cm\(^{-1}\) lower value.

9. Regions of 810-840 cm\(^{-1}\), 800-820 cm\(^{-1}\) and 780-800 cm\(^{-1}\) are claimed to be R\(_1\)R\(_2\)C=CHR\(_3\) out-of-plane deformation of non-strained, weakly strained (e.g. cyclohexene derivatives) and strongly strained systems respectively. The extinction coefficients increase in this direction from 30 \(\pm\) 10 up to 90 (as found for \(\alpha\)-pinene).

10. A band close to 950 cm\(^{-1}\) has been assigned to a O(CO)-CH\(_3\) stretching or bending typical for acetates only.

11. Weak bands at 730-735 and 738-744 cm\(^{-1}\) have been assigned to a CH\(_2\) rocking frequency for 3 and 2 adjacent CH\(_2\) groups respectively.

12. Isopropyl as well as isopropylidene groups absorb near 1190-1160 and 850 cm\(^{-1}\).

13. A doublet near 1110 and 1090 cm\(^{-1}\) (sometimes a singlet) has been assigned to =C-CH\(_3\) stretching or in-plane deformation. Finally, for a discussion of the cis/trans isomerism, which is said to exist at the R\(_1\)R\(_2\)C=CHR\(_3\) groups of nerol and geraniol, one is referred to Chapters V and VI.
### Table IV.1 Infrared Data of Tertiary Monoterpene Alcohols

<table>
<thead>
<tr>
<th>Vibration - Mode</th>
<th>Linalol</th>
<th>Dihydro-Linalol</th>
<th>Tetrahydro-Linalol</th>
</tr>
</thead>
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<td>O-H stretch</td>
<td>3590 m</td>
<td>3610 m 23</td>
<td>3608 33</td>
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<tr>
<td>free OH</td>
<td>3485 vs</td>
<td>3410 37</td>
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<tr>
<td>associated OH</td>
<td>3675 vs</td>
<td>3610 21 22$\delta$</td>
<td>3672 $\delta$ 21 22$\delta$</td>
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<tr>
<td>C-H stretch</td>
<td>3070 w</td>
<td>3090 w 188</td>
<td>3085 w 189</td>
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<td>=C-H$_{ax}$</td>
<td>3090 m</td>
<td>3075 w 188</td>
<td>3090 w 189</td>
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<td>-CH$_3$ asymmetric stretch</td>
<td>~3010 w</td>
<td>2920 w 102$\delta$</td>
<td>~3015 w 2920 w 102$\delta$</td>
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<td>2920 w 102$\delta$</td>
<td>2920 w 102$\delta$</td>
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<td>2855 s 89$\delta$</td>
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<td>-CH$_3$ out phase stretch</td>
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<td>2870 s 89$\delta$</td>
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<td>1754 m 4.1</td>
<td>1754 m 4.1</td>
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<td>1754 m 4.1</td>
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<td>1675 w 8.4</td>
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<tr>
<td>OH and asymmetric CH$_3$ def.</td>
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<td>_1550 w 8.4</td>
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<tr>
<td>-CH$_3$ in phase def.</td>
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<td>_1550 w 8.4</td>
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<tr>
<td>symmetric CH$_3$ def.</td>
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<td>C-CH$_3$ stretch</td>
<td>1112 s 31 20</td>
<td>1112 s 31 20</td>
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</tr>
<tr>
<td>of tertiary alcohols</td>
<td>1112 s 31 20</td>
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<tr>
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<td>RRC$_{12}$CH$_3$ group</td>
<td>1504 vs 19.1</td>
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<td>R$<em>{1}$R$</em>{2}$-CH$_3$CH$_2$ group</td>
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### Table IV.2 Infrared Data of Primary Alcohols

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<tr>
<th>Vibration - Mode</th>
<th>Nerol</th>
<th>Geraniol</th>
<th>Citronellol</th>
<th>Tetrahydro-Geraniol</th>
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</thead>
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<tr>
<td>O-H stretch</td>
<td>3609 m 17</td>
<td>3619 m 31</td>
<td>3619 m 30</td>
<td>3619 m 30</td>
</tr>
<tr>
<td>free OH</td>
<td>3234 wa 27</td>
<td>3235 wa 47</td>
<td>3235 wa 47</td>
<td>3235 wa 47</td>
</tr>
<tr>
<td>associated OH</td>
<td>3234 wa 27</td>
<td>3235 wa 47</td>
<td>3235 wa 47</td>
<td>3235 wa 47</td>
</tr>
<tr>
<td>C-H stretch</td>
<td>1504 vs 19.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>=C-H$_{ax}$</td>
<td>1504 vs 19.1</td>
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</tr>
<tr>
<td>-CH$_3$ asymmetric stretch</td>
<td>1504 vs 19.1</td>
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<td></td>
<td></td>
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<tr>
<td>-CH$_3$ symmetric stretch</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>-CH$_3$ out phase stretch</td>
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<td></td>
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<tr>
<td>C-C stretch</td>
<td>1680 m 27 21</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>symmetric CH$_3$ def.</td>
<td>1466 s 71</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-CH$_3$ stretch</td>
<td>1076 s 89</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>of primary alcohols</td>
<td>1076 s 89</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-H out of phase deformation</td>
<td>1076 s 89</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R$<em>{1}$R$</em>{2}$-CH$_3$CH$_2$ group</td>
<td>1076 s 89</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Skeletal vibrations</td>
<td>1076 s 89</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>of isopropyl group</td>
<td>1076 s 89</td>
<td></td>
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</tr>
<tr>
<td>=C-C$_{=}$CH$_3$ stretch or def.</td>
<td>1076 s 89</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>see C-CH$_3$ stretch</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>C-CH$_3$ rocking deform.</td>
<td>737 w 737 w</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n = 2</td>
<td></td>
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<td></td>
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<tr>
<td>n = 3</td>
<td></td>
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</table>
### Table IV.3  Infrared data of Tertiary monoterpene Acetate

<table>
<thead>
<tr>
<th>VIBRATION - MODE</th>
<th>LINALYL ACETATE</th>
<th>DIONHYDROLINALYL ACETATE</th>
<th>TETRAHYDROLINALYL ACETATE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( v (cm^{-1}) )</td>
<td>( \nu_{11} ) ( \frac{cm}{Mol} )</td>
<td>( \Delta v ) ( \frac{cm}{Mol} )</td>
</tr>
<tr>
<td>C-H stretch</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( =C-H ) stretch</td>
<td>3050 w</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( =C-H ) stretch</td>
<td>-2000 w</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( CH_2 ) asymm. stretch</td>
<td>2018 s</td>
<td>2920 s</td>
<td>2930 s</td>
</tr>
<tr>
<td>( CH_2 ) in phase stretch</td>
<td>2454 s</td>
<td>2962 s</td>
<td>2960 s</td>
</tr>
<tr>
<td>( CH_3 ) out phase stretch</td>
<td>1730 vs</td>
<td>440 16</td>
<td>1755 vs 55 19</td>
</tr>
<tr>
<td>C-O stretch</td>
<td>1673 w 14 4.5</td>
<td>~1675 w</td>
<td>~1675 w</td>
</tr>
<tr>
<td>CH_2 and CH_3 deformation</td>
<td>1463 m 20 16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH_2 and CH_3 deformation</td>
<td>1243 vs 390 30.5</td>
<td>1274 vs 475 23</td>
<td>1157 vs 460 28</td>
</tr>
<tr>
<td>Skeletal vibrations</td>
<td>1172 w 41 7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( =C-H ) out of plane deformation</td>
<td>916 s 125 10</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( =C-H ) out of plane deformation</td>
<td>1091 m 24 ~50</td>
<td>1091 m 24 ~50</td>
<td>1172 m 24 ~50</td>
</tr>
</tbody>
</table>

### Table IV.4  Infrared data of Primary monoterpene Acetate

<table>
<thead>
<tr>
<th>VIBRATION - MODE</th>
<th>NERYL ACETATE</th>
<th>GERANYL ACETATE</th>
<th>CITRONELLYL ACETATE</th>
<th>TETRAHYDROLINALYL-GERANYL ACETATE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( v (cm^{-1}) )</td>
<td>( \nu_{11} ) ( \frac{cm}{Mol} )</td>
<td>( \Delta v ) ( \frac{cm}{Mol} )</td>
<td>( v (cm^{-1}) )</td>
</tr>
<tr>
<td>C-H stretch</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( =C-H ) stretch</td>
<td>-2035 w</td>
<td>-2035 w</td>
<td>-2035 w</td>
<td>-2035 w</td>
</tr>
<tr>
<td>( CH_2 ) asymm. stretch</td>
<td>2059 s</td>
<td>2924 s</td>
<td>2923 s</td>
<td>2059 s</td>
</tr>
<tr>
<td>( CH_2 ) in phase stretch</td>
<td>2352 s</td>
<td>2960 s</td>
<td>2958 s</td>
<td>2352 s</td>
</tr>
<tr>
<td>( CH_3 ) out phase stretch</td>
<td>2400 m</td>
<td>2960 s</td>
<td>2958 s</td>
<td>2400 m</td>
</tr>
<tr>
<td>C-O stretch</td>
<td>1764 vs 500 17.4</td>
<td>1742 vs 490 17.5</td>
<td>1747 vs 550 16</td>
<td>1743 vs 620 16</td>
</tr>
<tr>
<td>CH_2 and CH_3 deformation</td>
<td>1671 m 24 20</td>
<td>1671 m 24 20</td>
<td>1671 m 24 20</td>
<td>1671 m 24 20</td>
</tr>
<tr>
<td>CH_2 and CH_3 deformation</td>
<td>1245 m 127 11</td>
<td>1245 m 127 11</td>
<td>1245 m 127 11</td>
<td>1245 m 127 11</td>
</tr>
<tr>
<td>Skeletal vibrations</td>
<td>1100 m 60 60</td>
<td>1100 m 60 60</td>
<td>1100 m 60 60</td>
<td>1100 m 60 60</td>
</tr>
</tbody>
</table>

---

Due to the limitations of this text format, the table is not fully rendered. It appears to be a continuation of the infrared data, possibly for a different group of terpene acetates, but the full content is not fully visible. Additional information and data may be available in the full document.
### Table IV-5 Infrared Data of Monoterpene Hydrocarbons

<table>
<thead>
<tr>
<th>Mode</th>
<th>α-PINENE</th>
<th>β-PINENE</th>
<th>LIMONENE</th>
<th>MYRcene</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-H stretch</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>α-C-H stretch</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>β-C-H stretch</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-H asymmetrical stretch</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-H in plane stretch</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-H symmetrical stretch</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-H out of plane stretch</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C=C stretch</td>
<td>1665 w</td>
<td>1642 s</td>
<td>1672 w</td>
<td>1655 m</td>
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<tr>
<td>R3C=C=CHR2</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>R3C=C=CHR2</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>C=H and CH3 deformations</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH3 and asymm. CH3 def.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>α-CH3 in plane def.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>symmetrical CH3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>α-CH3 out of plane def.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R8C=CHR2</td>
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<td></td>
</tr>
<tr>
<td>R8C=CHR2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Skeletal vibrations</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-H of isopropyl</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>C-H of isopropyl</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C=C-H stretch or bend.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(CH3) rocking deform.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6-membered ring</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- α: 
- β: 
- v: vibration mode
- cm\(^{-1}\): wavenumber
FIGURE IV-5
NEROL

FIGURE IV-6
CITRONELLOL
**Figure IV-7**

TETRAHYDROGERANIOL

**Figure IV-8**

LINALYL ACETATE
Figure IV-9
Dihydrolinalyl acetate

Figure IV-10
Tetrahydrolinalyl acetate
IV-3. The ultraviolet spectra

As most of the present substances, containing at least one C=C bond, proved to have a \( \lambda_{\text{max}} \) close to 190 nm, neither the position of \( \lambda_{\text{max}} \) nor \( \epsilon_{\text{max}} \) could be determined with much certainty. It was therefore tried whether \( \epsilon \)'s measured at one selected wavelength could provide some useful information. In Table IV-8 \( \epsilon \)'-values measured at 190 and 200 nm are tabulated, as well as \( \lambda_{\text{max}} \) and \( \epsilon_{\text{max}} \) whenever they could be estimated.

In figure IV-19, the UV absorption spectra of geraniol (1), citronellol (2) and tetrahydrogeraniol (3) have been reproduced to give an impression of the actual shape of such absorption bands.

All the compounds were measured in n-heptane, in 2-mm fused-silica cells. The Cary 14 spectrophotometer was used for all the measurements. Below 190 nm a stray-light correction had to be made. The average accuracy of the extinction coefficients quoted, is presumably not better than \( \pm 5\% \).

### Table IV-8

<table>
<thead>
<tr>
<th>Substance</th>
<th>( \lambda_{\text{max}} ) (nm)</th>
<th>( \epsilon_{\text{max}} )</th>
<th>( \epsilon_{200} )</th>
<th>( \epsilon_{100} )</th>
<th>Number of C=C bonds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linalol</td>
<td>188</td>
<td>15,000</td>
<td>8,700</td>
<td>14,500</td>
<td>2</td>
</tr>
<tr>
<td>Dihydrrolinalol</td>
<td>190 ± 1</td>
<td>10,000</td>
<td>7,400</td>
<td>10,000</td>
<td>1</td>
</tr>
<tr>
<td>Tetrahydrolinalol</td>
<td>195</td>
<td>15,500</td>
<td>8,900</td>
<td>15,500</td>
<td>2</td>
</tr>
<tr>
<td>Linalyl acetate</td>
<td>180 ± 1</td>
<td>14,700</td>
<td>7,100</td>
<td>14,700</td>
<td>1</td>
</tr>
<tr>
<td>Dihydrrolinalyl acetate</td>
<td>190 ± 1</td>
<td>250</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Geraniol</td>
<td>180 ± 1</td>
<td>19,000</td>
<td>16,000</td>
<td>17,000</td>
<td>2</td>
</tr>
<tr>
<td>Nerol</td>
<td>192 ± 1</td>
<td>18,500</td>
<td>15,000</td>
<td>15,000</td>
<td>2</td>
</tr>
<tr>
<td>Citronellol</td>
<td>190 ± 1</td>
<td>20,000</td>
<td>7,900</td>
<td>10,000</td>
<td>1</td>
</tr>
<tr>
<td>Tetrahydrogeraniol</td>
<td>180 ± 1</td>
<td>20,700</td>
<td>17,700</td>
<td>20,000</td>
<td>2</td>
</tr>
<tr>
<td>Geranyl acetate</td>
<td>180 ± 1</td>
<td>20,000</td>
<td>16,600</td>
<td>19,000</td>
<td>2</td>
</tr>
<tr>
<td>Neryl acetate</td>
<td>180 ± 1</td>
<td>20,000</td>
<td>16,600</td>
<td>19,000</td>
<td>2</td>
</tr>
<tr>
<td>Citronellyl acetate</td>
<td>192 ± 1</td>
<td>6,700</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tetrahydrogeranyl acetate</td>
<td>200</td>
<td>5,000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \alpha )-pinene</td>
<td>180 ± 1</td>
<td>5,000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \beta )-pinene</td>
<td>180 ± 1</td>
<td>10,000</td>
<td>10,000</td>
<td>10,000</td>
<td>2</td>
</tr>
<tr>
<td>Limonene</td>
<td>190 ± 1</td>
<td>17,000</td>
<td></td>
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<td>2</td>
</tr>
<tr>
<td>Myrcene</td>
<td>190</td>
<td>14,500</td>
<td></td>
<td></td>
<td>1</td>
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<tr>
<td></td>
<td>225</td>
<td>10,500</td>
<td></td>
<td></td>
<td>2</td>
</tr>
</tbody>
</table>

The results can be summarized as follows:

1. Non-conjugated trisubstituted C=C groups appear to have a \( \lambda_{\text{max}} \) between 190 and 193 nm. For purely hydrocarbon type of groups \( \lambda_{\text{max}} = 190 \pm 1 \text{ nm} \) and \( \epsilon_{\text{max}} = 11,000 \pm 1,000 \) is found. When oxygen is present on a \( C\beta \) atom, \( \lambda_{\text{max}} = 192 \pm 1 \text{ nm} \) and \( \epsilon_{\text{max}} = 8,000 \pm 1,000 \).

2. Monosubstituted C=C groups absorb below 188 nm. Their extinction coefficient at 190 nm amounts to about 4,000.
3. The best way to count the number of C=C groups of non-cyclic, non-conjugated ethylene derivatives, is in our opinion - UV measurements at 190 nm.

**Figure IV.19**

**IV-4. The NMR spectra**

In this section the NMR spectra of 18 terpenes will be discussed. All the
samples have been measured in the undiluted liquid state, unless stated otherwise. Chemical shifts are given relative to TMS (tetramethylsilane), of which a small amount was added to each sample. Chemical shifts will be recorded as \( r \) values, \( r \) being defined by

\[
r = 10 - \frac{\Delta \nu \cdot 10^6}{\nu_0}
\]

Here \( \Delta \nu \) stands for the chemical shift expressed in cycles per second (cps), relative to TMS; \( \nu_0 \) is the oscillator frequency being 40 Mcps for all the measurements.

Coupling constants \( J \) will always be given in cps. The accuracy of the instrument amounted to \( \pm 0.2 \) cps for a single measurement, and the coupling constants to be quoted will usually have this accuracy. As a rule, chemical shifts have a slightly less accuracy, mainly for two reasons. First of all, many lines are broadened (either by small relaxation times or by overlap of nearly equivalent groups or by long-range spin-spin coupling with small coupling constants), so that the actual frequency of maximum absorption cannot be determined with great precision. Secondly, we hardly ever deal with A X systems, but nearly always with A K, if not A B systems. Under these conditions, where the chemical shift difference between two (or more) groups of equivalent protons approaches the coupling constant(s) — with which those groups couple — the centre of any spin-spin multiplet no longer coincides with the frequencies at which they would absorb in case of zero spin-spin coupling. Under circumstances of such severe interaction (see e.g. the A B K system of the isolated vinyl groups or the A \(_2\) B \(_3\) system of the isolated ethyl groups) it will be tried to disentangle the complex patterns, which result from this interaction, in order to calculate the exact values for \( r \) and \( J \). In many other systems, however, the result of the interaction between \( r \) and \( J \) is only a change in intensity ratios, and a slight shift of the centres of the absorbing groups (towards each other). With these considerations in mind, \( r \) values will be quoted with an accuracy of \( \pm 0.01 \), being equivalent to \( \pm 0.4 \) of a cycle for the 40 Mc measurements.

Further experimental details will be given in Chapter VII.

On the next pages, the NMR spectra have been reproduced. Magnetic field increases from left to right, abciss is in \( r \) values. Spectral parts with much fine structure are reproduced on an expanded scale. Like the discussion of the infrared spectra, the distinguishable groups will be discussed one by one.

\(-\text{CH}_2-\text{CH}_3\)

This group is present in dihydro- and tetrahydrolinalol and their acetates.
They constitute four examples of isolated $A_2B_3$ groups. The methyl parts of the spectra correspond quite well with that calculated by Arnold\(^*\) in a second order perturbation theory. Values of 9.13 for the alcohols and 9.18 for the acetates have been evaluated. From the asymmetry of the multiplet (especially for the alcohols) it is seen that the second order perturbation is not completely adequate. For this reason the quoted $r$ values (especially for the alcohols) will be a little too low. A coupling constant $J_{AB} = 7.2$ cps has been derived from the four spectra

![\text{Structure}]

This structure, present in tetrahydrolinalol, citronellol and tetrahydrogeraniol, as well as in their acetates, is found as a slightly asymmetrical doublet with $r = 9.11$ and $J = 4.8-4.9$ cps. The asymmetry is due to the fact that this structure is not a pure $A_3X$ system, but rather an $A_3K$ system. The methine proton probably absorbs near $r = 8.5$, so that the $J/\Delta
u$ ratio is in the order of 0.2. In such a case the methyl absorption consists of two doublets instead of one. The two lines of each doublet will lie so closely together, however, that they will be hardly separated, if at all. The width of nearly 2 cps for each of the lines of the experimentally found doublet indicates this double doublet character. In citronellol (and acetate), only one such a CH\(_3\) group is present, in tetrahydrolinalol (and acetate) two, and in tetrahydrogeraniol (and acetate) three, a fact which is confirmed by the integrated spectra. Whether one, two or three such groups are present, the doublet does not change its $r$ value, and even the line widths remain the same, which proves the exact overlap of these CH\(_3\) signals, although they are not completely equivalent.

![\text{Structure}]

This remarkable group is found in the pinenes, where it is part of the cyclobutane system. Although in 1,1 dimethyl cyclobutane itself the two CH\(_3\) groups would be equivalent, they are not so in the pinenes, because of a spatial effect. One of the CH\(_3\) groups has a much smaller average distance to the C=C group as compared to the other. The latter will have a $r$ value near 9.1-9.3, the normal region for saturated hydrocarbon CH\(_3\) groups. Indeed, $r$ values of 9.15 ($\alpha$-pinene) and 9.27 ($\beta$-pinene) have been found for this CH\(_3\) group; 8.73 ($\alpha$-pinene) and 8.77 ($\beta$-pinene) for the other one. This $r$ value of about 8.7 is in fact an average of two $r$ values, corresponding to each of the conformational possibilities of the 6-membered ring. The original two absorptions are averaged by the rapid interchange between the two conformations.
This group is frequently encountered in terpene compounds. The two CH groups are not equivalent; the one cis to the olefinic proton will absorb at slightly lower $r$. Long-range coupling between the olefinic proton and the two CH$_3$ groups may be expected, the cis coupling constant being approximately half that of the trans-coupling constant. A further slight splitting can be expected because of the A$_3$K character. As a result each of the CH$_3$ signals will have to consist of a closely spaced quartet of lines which are nearly of the same intensity. In most cases only two rather broad peaks are found instead of the expected two quartets; $r$ values of 8.33 and 8.40 for the two CH$_3$ absorptions may be quoted. The occurrence of two such bands forms a strong evidence for a 2-methyl butene-2 derivative.

The best examples are found in dihydrolinalol, citronellol, their acetates and myrcene. In some other compounds like nerol, geraniol and their acetates the group is present as well, but is somewhat obscured by the absorption of the very similar grouping CH$_2$-HC=C(CH$_3$)-CH$_2$.

The question whether the difference between a cis or trans structure can be seen from the methyl absorption, will be considered in Chapter VI.

The group in question is also present in $\alpha$-pinene ($r = 8.37$) and limonene, now no longer overlapped by a isopropylidene absorption. In the case of limonene, however, another methyl absorption H$_2$C=C(CH$_3$)-CH causes a complex pattern, which could not be analyzed with much certainty.

$$\text{CH}_3-\text{CR}_1\text{R}_2-\text{OR}_3$$

This structure is present in linalol, dihydro- and tetrahydrolinalol and their acetates. $R_1$ is always a saturated alkyl group, $R_2$ may be a C=C group. The extra deshielding, if such a C=C group is present in the $\beta$, $\gamma$ site or if OH is replaced by COOCH$_3$, is clearly seen from Table IV-9.

<table>
<thead>
<tr>
<th></th>
<th>$R_1$</th>
<th>$R_2$</th>
<th>$T$</th>
<th>$\text{CH}_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrahydrolinalol</td>
<td>C=C</td>
<td>ally</td>
<td>H</td>
<td>8.00</td>
</tr>
<tr>
<td>Dihydrolinalol</td>
<td>C=C</td>
<td></td>
<td>H</td>
<td>8.65</td>
</tr>
<tr>
<td>Tetrahydrolinalol acetate</td>
<td>C=C</td>
<td></td>
<td>COOCH$_3$</td>
<td>8.34</td>
</tr>
<tr>
<td>Dihydrolinalol acetate</td>
<td>C=C</td>
<td></td>
<td>COOCH$_3$</td>
<td>8.63</td>
</tr>
<tr>
<td>Linalol</td>
<td>C=C</td>
<td></td>
<td>H</td>
<td>8.74</td>
</tr>
<tr>
<td>Linalyl acetate</td>
<td>C=C</td>
<td></td>
<td>COOCH$_3$</td>
<td>8.49</td>
</tr>
</tbody>
</table>
CHAPTER IV

Apparently the replacement of OH by OCHCH$_3$ results in a $\Delta \tau = -0.26 \pm 0.01$ and replacement of C-C by C=C results in a $\Delta \tau = -0.15 \pm 0.01$. When both substitutions occur, a $\Delta \tau = -0.41 \pm 0.02$ might be expected. This is in good agreement with the experimentally found $\Delta \tau = -0.40$ for linalyl acetate. This kind of additivity of substituent-effect on chemical shift is known as Shoolery's rule.

$\text{O-C-CH}_3$

The acetate methyl group is easily recognized by its long relaxation time, resulting in characteristic relaxation wiggles in the spectra. One of the reasons for this is the isolated position of the acetate protons, the nearest neighbouring protons are at a distance of 5 or 6 chemical bonds. For the same reason the chemical shift is quite independent of substitutions on the alcohol part of the molecule. $\tau = 8.06 \pm 0.02$ is found for all acetates.

$R_1-\text{CH}_2-0R_2$

This structure can easily be found as its frequency is about halfway between olefinic proton and alkyl proton absorption. This lower $\tau$ value as compared with alifatic hydrocarbon CH$_2$ $\tau$ values, is due to the deshielding action of the electronegative oxygen atom to which it is attached. $R_1$ may be a $\text{C-CH}_2-$ or a $\text{C}=\text{H}-$ group and $R_2$ is either $\text{H}$ or -COCH$_3$.

The actual $\tau$ values (and coupling constant) are given in Table IV-10.

$\text{TABLE IV-10}$

<table>
<thead>
<tr>
<th>$R_1$</th>
<th>$R_2$</th>
<th>$\tau$ (ppm)</th>
<th>$J$ (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrahydrogeranlol</td>
<td>-C-H$_2$-</td>
<td>6.44</td>
<td>6.4</td>
</tr>
<tr>
<td>Citronellol</td>
<td>-N</td>
<td>6.44</td>
<td>6.5</td>
</tr>
<tr>
<td>Tetrahydropinyl acetate</td>
<td>-COCH$_3$</td>
<td>5.94</td>
<td>5.0</td>
</tr>
<tr>
<td>Citronylyl acetate</td>
<td>-COCH$_3$</td>
<td>5.98</td>
<td>6.8</td>
</tr>
<tr>
<td>Geraniol</td>
<td>-N</td>
<td>5.96</td>
<td>6.4</td>
</tr>
<tr>
<td>Nerol</td>
<td>-N</td>
<td>5.99</td>
<td>6.8</td>
</tr>
<tr>
<td>Gennafoyl</td>
<td>-COCH$_3$</td>
<td>5.90</td>
<td>7.2</td>
</tr>
<tr>
<td>Neryl acetate</td>
<td>-COCH$_3$</td>
<td>5.90</td>
<td>7.0</td>
</tr>
</tbody>
</table>

The effect on the chemical shift when OH is replaced by OCOCH$_3$ amounts to $\Delta \tau = -0.48 \pm 0.03$. Substituting C-C by C=C causes a $\Delta \tau = -0.46 \pm 0.03$. When both effects occur, a $\Delta \tau = -0.94 \pm 0.06$ might be calculated. From neryl (geranyl) acetate and citronellol, a $\Delta \tau = -0.94$ is experimentally found, in exact agreement with the calculated value.
Other $\text{CH}_2$ absorptions

There is little hope that other $\text{CH}_2$ groups can be identified, this being a results of the non-equivalence of the $\text{CH}_2$ groups and the multiplet structures to be expected. Dihydrolinalol, for instance, will have $\text{CH}_2$ absorption formed by an overlap of the A part of an $A_2B_3$ system (6 lines), the A part of an $A_2B_2$ system (7 lines) and the B part of an $A_2B_2K$ (12 lines).

Only if the terpene molecule is completely hydrogenated, three $\text{CH}_2$ groups become nearly equivalent, resulting in a (rather broad) band near $\tau = 8.7$. Nerol, geraniol and their acetates show a similar broad absorption near $\tau = 7.9 \pm 0.1$, characteristic for a number of nearly equivalent C=C-$\text{CH}_2$ groups. The centre of the $\text{CH}_2$ absorptions of the four hydrocarbon terpenes is also found near $\tau = 7.9$.

\[
\begin{align*}
\text{C} & \text{CH-C} \\
\text{C} &
\end{align*}
\]

The methine group usually absorbs near $\tau = 8.5$ and it is only if the $\text{CH}_2$ absorptions collaps into one band (like discussed in the preceding paragraph) that the methine proton absorption will become visible, although the signal is very weak because of its multiple spin-spin coupling.

\[
\begin{align*}
2 & \text{H} \text{C-C-H} \\
 & \text{H} \\
 & \text{H}
\end{align*}
\]

This vinyl structure is present in linalol and linalylacetate, which constitute ideal examples of isolated vinyl groups, because the C$_\beta$ atom is tri-substituted. The two spectra look very much like hybrids between $AB_2$ and $XAB$ systems. Especially in linalyl acetate the left-hand quartet (of the H$^2$ proton) is very similar to that of an $AB_3$ system with $1/\Delta\nu = 0.3$. The right-hand side (of H$^3$ and H$^4$ protons) is much like two quartets, and reminds both of the quartet to be expected for an $AB$ system, as well as of the eight lines to be expected for $XAB$ systems. For linalol, indeed, six X lines are present. So, the spectra may preferably be described as $ABK$ systems.

From the reproduced spectra the following data could be derived: first figure for linalol and second for linalyl acetate.

\[
\begin{align*}
\tau_4 &= 4.62 \ (4.60) \quad J_{24} = 17.2 \ (18.4) \ \text{cps} \\
\tau_5 &= 5.03 \ (5.00) \quad J_{23} = 10.1 \ (9.2) \ \text{cps} \\
\tau_2 &= 4.95 \ (4.98) \quad J_{34} = 2.6 \ (2.0) \ \text{cps}
\end{align*}
\]

These figures must be regarded as approximations, because all the separations always include both chemical shifts and coupling constants. In myrcene there is also a vinyl group present, but while the K part of it is well shown,
the AB part is overlapped by an $R_1 R_2 C=CH_2$ absorption. Nevertheless, the following data were calculated: $\tau_2 = 3.59$, $\tau_3 = 4.97$, $\tau_4 = 4.79$ and $J_{23} = 17.5$, $J_{24} = 10.7$ and $J_{34} = 1.8$ cps. The coupling constants and the $\Delta \tau$ value are in good agreement with those obtained from linalol and linalyl acetate, but apparently the signal as a whole has shifted to a 1 unit lower $\tau$ value.

\[
\text{C} \text{C} \equiv \text{C} \text{H} \\
\text{C} \text{H}
\]

This group is present in $\beta$-pinene, limonene and myrcene, and absorbs at $\tau = 5.37$, $\tau = 5.31$ and $\tau = 5.01$ respectively, the latter value somewhat lowered by the conjugation with the vinyl group. All three bands show much fine structure, caused by long-range coupling and by the fact that the two olefinic protons will have slightly different chemical shifts. The limonene peak will consist of 16 lines of which only four are resolved; myrcene and $\beta$-pinene will have 12 lines, which are again only partly or not resolved.

\[
\text{C} \text{C} \equiv \text{C} \text{H} \\
\text{C} \text{C}
\]

This group is typical for all isoprenoidal compounds, and in some of the present terpenes even two of these groups are present, which overlap to some extent. Dihydrolinalol, citronellol and their acetates which have only one $(\text{CH}_3)_2 C=\text{CHR}_3$ group ($R_3$ saturated alkyl group), show the olefinic proton at $4.89 \pm 0.01$, with a coupling constant $J \sim 6.7$ cps to the neighbouring $\text{CH}_2$ group and long-range coupling to the two $\text{CH}_3$ groups with $J = 1-2$ cps. Nerol, geraniol, and their acetates show besides the isopropylidenic group also an $R_1 (\text{CH}_2)C=\text{CH}-\text{CH}_2-O$ group with $\tau$ between 4.60 and 4.67. These lower $\tau$ values are probably caused by the oxygen atom of the $\text{CH}_2-O$-part. Again coupling constants of about 6.7 cps (to the $\text{CH}_2$ group) and 1-2 cps (to the $\text{CH}_3$ and $R_1$ group) are found. In Chapter VI this absorption will be discussed again, in order to elucidate the cis/trans isomerism of nerol and geraniol.

Myrcene, linalol and linalyl acetate have also an isopropylidene group, but its absorption is completely obscured by the vinyl proton absorption. Limonene ($\tau = 4.62$) and $\alpha$-pinene ($\tau = 4.8$) are two further examples.

\[
\text{C}=\text{O} \text{H}
\]

The three tertiary alcohols linalol, dihydro- and tetrahydrolinalol show a single peak at $\tau = 6.45$, $\tau = 6.52$ and $\tau = 6.44$, while the four primary alcohols (geraniol, nerol, citronellol and tetrahydrogeraniol) absorb in a
similar way at \( r = 5.26, \quad r = 5.33, \quad r = 5.15 \) and \( r = 5.04 \).

Apparently, the primary alcohols absorb at about 1.2 lower \( r \) value, most probable because of the stronger hydrogen bonding. This result is quite analogous to the difference in \( \nu (O-H) \) stretch of the infrared spectra already discussed.

In Table IV-11 and Table IV-12 the numerical data, both on \( r \) values and coupling constants have been collected.

**Table IV-12**

<table>
<thead>
<tr>
<th>Structure</th>
<th>Type of coupling</th>
<th>( J ) (ppm)</th>
<th>Derived from compound 1 of Table IV-11</th>
</tr>
</thead>
<tbody>
<tr>
<td>( -CH__CH_OH )</td>
<td>( J_{\text{CH}-\text{CH}} )</td>
<td>6.5 ( \pm ) 0.2</td>
<td>4, 5, 6, 7</td>
</tr>
<tr>
<td>( -CH__CH__CH_ )</td>
<td>( J_{\text{CH}-\text{CH}} )</td>
<td>6.8 ( \pm ) 0.3</td>
<td>2, 5, 12, 5, 4, 12, 21</td>
</tr>
<tr>
<td>( -CH__CH___CH_ )</td>
<td>( J_{\text{CH}-\text{CH}} )</td>
<td>7.0 ( \pm ) 0.4</td>
<td>11, 13, 23, 14</td>
</tr>
<tr>
<td>( H^+ - \text{C} - \text{C} - \text{H} )</td>
<td>( J_{\text{H}, \text{CH}} )</td>
<td>1.73 ( \pm ) 1.5</td>
<td>1, 6, 18</td>
</tr>
<tr>
<td>( H^+ - \text{C} )</td>
<td>( J_{\text{H}, \text{CH}} )</td>
<td>1.8 ( \pm ) 2.5</td>
<td>1, 6, 18</td>
</tr>
<tr>
<td>( \text{H}^+ \cdot \text{H} )</td>
<td>( J_{\text{H}, \text{CH}} )</td>
<td>1.2 ( \pm ) 2.0</td>
<td>1, 2, 4, 5, 6, 9</td>
</tr>
</tbody>
</table>

Some of the more important results can be summarized as follows:

1. The NMR technique enables to distinguish tertiary acetates like di- and tetrahydro linalylacetate on the one hand, and citronellyl- and tetrahydrogeranyl acetate on the other hand, because of the easily identifiable methyl absorption of the \(-CH\_2-CH\_3\) group, present in the former two substances only. Such a distinction cannot be made by means of the infrared technique.

2. \( \text{H}^+ \cdot \text{C} \cdot \text{C} \cdot \text{CH}_3 \) can be distinguished from \( \text{H}^+ \cdot \text{C} \cdot \text{C} \cdot \text{CH}_3 \) as the former has two \( =\text{C}-\text{CH}_3 \) methyls (the other group only one). The position of such a group (near \( r = 8.4 \)) differs much from that of other \( \text{CH} \) signals. Apart from integration data, the isopropylidene methyls appear as a doublet (0.05 ppm separation), while the methyl of the other group has a singlet signal. This differentiation enables to estimate the position of a trisubstituted ethylenic group in acyclic monoterpenes.
<p>| | | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Linalool</td>
<td>8.74</td>
<td>8.49</td>
<td>8.33</td>
<td>8.0-8.8</td>
<td>4.62</td>
<td>3.59</td>
<td>4.62</td>
</tr>
<tr>
<td>2. Dihydroinalool</td>
<td>8.69</td>
<td>9.11</td>
<td>8.39</td>
<td>8.36</td>
<td>8.05</td>
<td>4.90</td>
<td>4.90</td>
</tr>
<tr>
<td>3. Tetrahydroinalool</td>
<td>8.60</td>
<td>9.11</td>
<td>8.40</td>
<td>8.32</td>
<td>8.00</td>
<td>4.90</td>
<td>4.90</td>
</tr>
<tr>
<td>4. Geraniol</td>
<td>8.39</td>
<td>8.36</td>
<td>8.05</td>
<td>4.90</td>
<td>4.90</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5. Nerol</td>
<td>8.40</td>
<td>8.32</td>
<td>8.00</td>
<td>4.90</td>
<td>4.90</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6. Citronellol</td>
<td>9.11</td>
<td>9.11</td>
<td>8.40</td>
<td>8.33</td>
<td>6.44</td>
<td>7.5-8.8</td>
<td>4.90</td>
</tr>
<tr>
<td>8. Linalyl acetate</td>
<td>8.49</td>
<td>8.00</td>
<td>8.39</td>
<td>8.36</td>
<td>8.05</td>
<td>4.90</td>
<td>4.90</td>
</tr>
<tr>
<td>10. Tetrahydroinalyl ac.</td>
<td>8.64</td>
<td>9.12</td>
<td>8.15</td>
<td>8.41</td>
<td>8.33</td>
<td>5.50</td>
<td>7.9</td>
</tr>
<tr>
<td>11. Geranyl acetate</td>
<td>8.07</td>
<td>8.07</td>
<td>8.39</td>
<td>8.33</td>
<td>5.50</td>
<td>7.9</td>
<td>4.89</td>
</tr>
<tr>
<td>12. Nerly acetate</td>
<td>8.07</td>
<td>8.07</td>
<td>8.39</td>
<td>8.33</td>
<td>5.50</td>
<td>7.9</td>
<td>4.89</td>
</tr>
<tr>
<td>13. Citronellyl acetate</td>
<td>9.00</td>
<td>9.00</td>
<td>8.39</td>
<td>8.33</td>
<td>5.50</td>
<td>7.9</td>
<td>4.89</td>
</tr>
<tr>
<td>14. Tetrahydrogeranlyl ac.</td>
<td>9.11</td>
<td>9.11</td>
<td>8.05</td>
<td>8.33</td>
<td>5.50</td>
<td>7.9</td>
<td>4.89</td>
</tr>
<tr>
<td>15. α-pinene</td>
<td>8.15</td>
<td>8.73</td>
<td>8.37</td>
<td>8.73</td>
<td>8.37</td>
<td>7.9</td>
<td>4.61</td>
</tr>
<tr>
<td>16. β-pinene</td>
<td>8.27</td>
<td>8.27</td>
<td>8.37</td>
<td>8.37</td>
<td>8.37</td>
<td>7.9</td>
<td>4.61</td>
</tr>
<tr>
<td>17. Limonene</td>
<td>8.38</td>
<td>8.31</td>
<td>8.31</td>
<td>8.31</td>
<td>8.31</td>
<td>7.9</td>
<td>4.61</td>
</tr>
<tr>
<td>18. Myrcene</td>
<td>8.37</td>
<td>8.30</td>
<td>8.30</td>
<td>8.30</td>
<td>8.30</td>
<td>7.9</td>
<td>4.61</td>
</tr>
</tbody>
</table>
which again is impossible by infrared techniques. The same methyl
signal when integrated (as well as the integrated olefinic proton signal)
can reveal whether one or two trisubstituted ethylenic groups are present.

3. The methine proton, which is hardly ever seen in infrared spectra, can
be found by NMR by the spin-spin coupling with neighbouring protons.
For instance, the $\text{CH}_3\text{CH}_2\text{C}$ methine proton splits the methyl signal
into a doublet of 4.8 cps separation.

4. The methyl signal of $\text{CH}_3\text{COCH}_3$ (near $\tau = 8.90$) shows a $\Delta\tau =
-0.26$ on substituting H by COCH$_3$ in R$_3$, and a $\Delta\tau = -0.15$ on substituting C=C by a C=C in R$_1$. It was shown that these two substituent effects are additive.

5. In a similar way the methylene signal near $\tau = 6.44$ of $\text{R}_1\text{CH}_2\text{COCH}_3$ shows a $\Delta\tau = -0.48$ on substituting H by COCH$_3$ in R$_2$ and a $\Delta\tau = -0.46$ on substituting C=C by a $\beta,\gamma$ C=C in R$_1$. Again it was shown that these substituent effects are nicely additive.

6. A hydrocarbon type $\text{R}_1\text{R}_2\text{C}=\text{C}$ has been shown to absorb close to
$\tau = 4.90$ while the same olefinic proton absorbs near $\tau = 4.65$ in structures like $\text{R}_1\text{R}_2\text{C}=\text{CH}=\text{CH}_2$. Besides a coupling with the nearest protons of the R$_3$ group ($J \sim 6.7$ cps), long-range coupling ($J \sim 1-2$ cps) between the olefinic proton and the nearest protons of R$_1$ and R$_2$ has been observed.

7. Tertiary alcohols show the OH proton resonance at higher field ($\tau \sim 6.4$) as compared to primary alcohols ($\tau \sim 5.2$) — at least in the pure liquid state — this effect being ascribed to a difference in hydrogen bonding.
FIGURE IV-22
TETRAHYDROLINALOL

FIGURE IV-23
LINALYL ACETATE
**Figure IV.24**

Dihydrolinalyl acetate

**Figure IV.25**

Tetrahydrolinalyl acetate
FIGURE IV-26
GERANIOL

FIGURE IV-27
NEROL
FIGURE IV-32
CITRONELLYL ACETATE

FIGURE IV-33
TETRAHYDROGERANYL ACETATE
CHAPTER V

INFRARED AND NUCLEAR MAGNETIC RESONANCE SPECTRA OF TRISUBSTITUTED ETHYLENES (CIS-TRANS ISOMERISM IN PARTICULAR)

V-1. Introduction

Trisubstituted ethylenes of the general formula R₁HC=CH₂R₂ are frequently found among the polyisoprenoids, such as terpenoids, carotenoids, and steroids. If R₁ and R₂ do not form a ring while R₂ ≠ CH₃, cis-trans isomerism exists.

In two following sections, the IR and NMR spectra of seven olefins of the above mentioned general structure will be discussed. They are standard samples of the National Bureau of Standards as prepared under the American Petroleum Institute Research Project 44. Some relevant properties (as collected from the Selected Values of Properties API research project 44 Table 8a part 2) are given in Table V-1.

Relabelling has been done on account of a number of criteria to be developed in this Chapter. For all of these rules the pair A B gave the opposite results while the other test substances C+G gave results fitting exactly in all of those criteria which could be predicted theoretically. Only density and refractive indices of A and B suggest the original labelling.

An unambiguous definition of which isomer is "cis" and which is "trans" is obtained by considering the longest carbon chain across the double bond, and by establishing whether the two substituents in this chain are either in a "cis" or a "trans" position.

V-2. The infrared spectra

There are several ways to explore infrared spectra in order to find criteria for the cis-trans isomerism under study. Firstly we can employ the general features of the spectra; secondly one can look for frequency and intensity
shifts of "obvious" bands such as C=C stretch, =\text{C}^{-}\text{H} stretch and =\text{C}^{-}\text{H} out of plane deformation; thirdly there may be found second order effects on the substituents of the C=C band such as on the CH\text{2} and CH\text{3} stretching and deformation modes.

Lastly one may look for absorption bands which are unique for either of the two isomeric structures. Such vibrations will almost certainly occur, but they are difficult to detect and tricky to apply.

**General features of infrared spectra**

The number of normal vibrations is determined by the number of atoms constituting the molecule. Nevertheless the number of infrared bands of a cis-isomer will be larger than that of the corresponding trans-isomer. The trans-isomer has a higher symmetry, because of which it may have degenerate vibrations which are non-degenerate at the cis isomer, and secondly the higher symmetry may cause a lowering of certain transition moments, resulting in a decreased or almost zero intensity of such absorption bands.
This principle has been applied to the API substances and the results are shown in Table V-2.

**Table V-2**

<table>
<thead>
<tr>
<th></th>
<th>IR absorption bands (frequencies in cm⁻¹)</th>
<th>Found in &quot;trans&quot; and absent or much weaker in &quot;cis&quot; isomer</th>
<th>Excess number of &quot;cis&quot; bands over &quot;trans&quot; bands</th>
</tr>
</thead>
<tbody>
<tr>
<td>AB</td>
<td>cis and trans 1043, 1020, 905, 745, 749</td>
<td>1236, 1296</td>
<td>4 - 2 = 2</td>
</tr>
<tr>
<td></td>
<td>3-Me-benzene-3 957, 758</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CD</td>
<td>cis and trans 1058, 1097, 927, 764</td>
<td>1220, 746</td>
<td>4 - 2 = 2</td>
</tr>
<tr>
<td></td>
<td>3-Me-pentane-3 957, 754</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EF</td>
<td>cis and trans 1122, 1135, 1022</td>
<td>1074, 1045</td>
<td>7 - 5 = 2</td>
</tr>
<tr>
<td></td>
<td>3,4-DiMe-pentane-2 1019, 922, 782, 700</td>
<td>904, 914, 716</td>
<td></td>
</tr>
</tbody>
</table>

resulting in the first criterium:

1. Within an isomeric pair of trisubstituted ethylenes, the cis isomer will have the larger number of infrared absorption peaks.

**The C=C stretch, =C–H out-of-plane deformation and =C–H stretch of R₁HC=C(CH₃)R₂ substances.**

Correlations for these vibrations are known since long, and have been discussed amply by many authors. (Bellamy* for instance quotes some 25 references).

Nevertheless we have re-checked these correlations by collecting the data now available from the API infrared spectral data, the Sadtler collection of infrared spectra, and the Documentation of Molecular Spectra (DMS) system. Furthermore the data from an important paper by Barnard et al* have been included. The results of this complications will be used when appropriate.

**The C=C stretching frequency** of trisubstituted ethylenic hydrocarbons will be found between 1625 and 1695 cm⁻¹ (44) with an apparent extinction coefficient ε' between 2.3 and 11.0 (32).¹

With two exceptions, all noncyclic (28) and cyclohexenic (11) substances absorb between 1660 and 1682 cm⁻¹. Exceptional values are found for

¹) (number of observations is given between brackets).
Strain by ring formation or steric hindrance by bulky substituents seems to cause a lowering of the frequency. The sp² hybridization at the olefinic carbon atoms will be disturbed by the steric effects, in the sense that the olefinic bond will acquire more orbital character, leaving more, undirected s orbital character for the substituents resulting in a looser chemical bond and correspondingly in lower frequency. We have no explanation for the exceptional high value of $\nu = 1695\,\text{cm}^{-1}$ for $\Delta^3$-carene.

Apparent extinction coefficients $\epsilon'$ have also been determined giving an average value of $\epsilon' = 4.7$ for (21) non-cyclic and $\epsilon' = 3.8$ for (8) cyclic substances.

As the non-cyclic examples contain both cis and trans isomers and the cyclic substances are inherently "cis", it might be concluded that cis isomers have a lower C=C stretch intensity than the trans isomers, probably because of the steric hindrance, while on symmetry considerations one would have expected the opposite.

Although the variations both in frequency and in extinction coefficient are large (larger even than the differences between the averaged values quoted above) two additional rules may be given:

II. Within an isomeric pair of trisubstituted ethylenes, the C=C stretching frequency will be lowest for the cis-isomer; the difference increasing with the bulkiness of the substituents.

III. The intensity of the C=C stretching will be lowest for the cis isomer ($\epsilon' = 4$ for cis and $\epsilon' = 6$ for trans may serve as representative figures). These criteria are demonstrated by the infrared spectra between 1600 and 1750 cm⁻¹ of the three isomeric pairs of API samples, which are reproduced in Figure V-1. At first sight the 3-Me-hexenes-3 form an exception on rule III, but this in our opinion is due to an overtone of the =C-H out-of-plane deformation. In the spectra C, D, E and F this overtone is easily distinguishable from the C=C stretching absorption, being less intense and having a frequency very nearly twice the fundamental (see Table V-4).

In the spectra A and B the calculated position of the overtones is indicated by an arrow, and it is seen that for the 3-Me-cis-hexene-3 this overtone frequency nearly coincides with the C=C stretch. Assuming an $\epsilon' = 2$ for the overtone (see spectra C D E F) a corrected $\epsilon'$ value of about 4 for the 3-Me-cis-hexene-3 can be obtained.
Figure V.1
The absolute intensities $\int (\epsilon')^* \cdot d\nu \text{ (cm}^2 \text{ molecule}^{-1} \text{ sec}^{-1})$, have also been calculated. After correction for the overtone intensity rule III again applies. In Table V-3 frequencies, extinction coefficients and absolute intensities have been tabulated, including those of 3-Me-cis-hexene-2 (G).

**Table V.3**

<table>
<thead>
<tr>
<th>SUBSTANCE</th>
<th>C=C stretching frequency (cm⁻¹)</th>
<th>C=CH a.o.p. deformation 1st overtone frequency (cm⁻¹)</th>
<th>C=CH a.o.p. deformation fundamental frequency (cm⁻¹)</th>
<th>$\epsilon'$</th>
<th>$\int (\epsilon')^* \cdot d\nu$ (cm²/molecule sec⁻¹) integrated between 1620-1720 cm⁻¹</th>
<th>C=C stretching</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1673</td>
<td>near 1794</td>
<td>852</td>
<td>6.6</td>
<td>2.4</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>1669</td>
<td>near 1776</td>
<td>858</td>
<td>7.0</td>
<td>2.8</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>1678</td>
<td>1652</td>
<td>621</td>
<td>5.7</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>1674</td>
<td>1629</td>
<td>609</td>
<td>4.3</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>1666</td>
<td>1643</td>
<td>819</td>
<td>4.9</td>
<td>2.6</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>1607</td>
<td>1614</td>
<td>816</td>
<td>4.1</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>1679</td>
<td>1650</td>
<td>616</td>
<td>5.8</td>
<td>3.1</td>
<td></td>
</tr>
</tbody>
</table>

The C=C⁻ H out of plane vibration near 800 cm⁻¹

For 37 non-cyclic hydrocarbons an average value $\nu = 828$ cm⁻¹ (ranging from 801 to 850 cm⁻¹) has been found while for 15 strained systems (mono or bi-cyclic substances), $\nu$ equals 800 cm⁻¹ (ranging from 781 to 820 cm⁻¹). Although the two regions overlap, this correlation may be useful as a diagnostic tool, if handled with care.

ε' Ranges (for 39 examples) between 10 and 70 ($\epsilon' = 33$) and it was observed that high ε' values were found for the strongly strained molecules. For instance 2-Me-norbornene ($\epsilon' = 70$), Δ⁵-carene ($\epsilon' = 63$), α-thujene ($\epsilon' = 55$), gave the highest three ε' values.

Reverting to the API samples for the cis-trans isomer pairs the following criteria are suggested:

IV. Within an isomeric pair of trisubstituted ethylenes, the =C⁻ H out of plane deformation near 820 cm⁻¹ will be lowest for the cis isomer.

V. The cis-isomer will then show the lowest intensity.

These rules are demonstrated by the IR spectra near 820 cm⁻¹ of the seven API samples mentioned. Numerical data are given in Table V-4.
A STUDY IN MONOTERPENE CHEMISTRY BY PHYSICAL METHODS

Table V-4

\[ \text{Out-of-plane vibration data} \]

<table>
<thead>
<tr>
<th>Substance</th>
<th>( \nu ) ( \text{cm}^{-1} )</th>
<th>( \epsilon' )</th>
<th>( \Delta \nu ) ( \text{cm}^{-1} )</th>
<th>Absolute intensity ( \text{10}^9 ) ( \text{f (\nu)} \text{ cm}^{-2} \text{ cmol}^{-1} \text{ cm}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A 3-Me-trans-hexene-3</td>
<td>852</td>
<td>42</td>
<td>11.7</td>
<td>5.7</td>
</tr>
<tr>
<td>B 3-Me-cis-hexene-3</td>
<td>838</td>
<td>43.1</td>
<td>10.3</td>
<td>6.8</td>
</tr>
<tr>
<td>C 3-Me-trans-pentene-2</td>
<td>821</td>
<td>47.3</td>
<td>11.9</td>
<td>7.6</td>
</tr>
<tr>
<td>D 3-Me-cis-pentene-2</td>
<td>809</td>
<td>56</td>
<td>26.7</td>
<td>11.7</td>
</tr>
<tr>
<td>E 3,4-dime-trans-pentene-2</td>
<td>791</td>
<td>79</td>
<td>11.1</td>
<td>14.4</td>
</tr>
<tr>
<td>F 2,4-dime-cis-pentene-2</td>
<td>906</td>
<td>56.8</td>
<td>14.5</td>
<td>10.8</td>
</tr>
<tr>
<td>G 3-Me-cis-hexene-2</td>
<td>810</td>
<td>26.7</td>
<td>17.3</td>
<td>6.0</td>
</tr>
</tbody>
</table>

The \( \text{C-H} \) stretching near 3030 cm\(^{-1}\)

Rule II, stating that cis isomers will have a lower \( \text{C=C} \) stretching frequency as compared to trans, directed the attention to the \( \text{C-H} \) stretching frequency as well. When the explanation given for rule II is correct then the \( \text{C-H} \) stretching frequency must be highest for the cis isomer as the increased s character of the \( \text{C-H} \) bond will increase its strength and hence its frequency.

Now with most instruments (equipped with NaCl prism monochromator) hardly anything can be seen about this band except sometimes a slight inflection point on the slope of the \( \text{CH}_3 \) and \( \text{CH}_2 \) absorption bands centered near 2900 cm\(^{-1}\).

The resolution theoretically obtainable with such equipment will be not better than 20 cm\(^{-1}\) at 3000 cm\(^{-1}\). So therefore a grating was installed in the instrument and now a theoretical resolution of 2 cm\(^{-1}\) could be obtained.

In this way the presence of the 3030 cm\(^{-1}\) band was clearly revealed. Surprisingly, however, another band near 3050 cm\(^{-1}\) was resolved now as well, although being even much weaker than the 3030 cm\(^{-1}\) band. We have no straightforward explanation for the 3050 band. The 3050 band was found to be absent in the hydrogenated analogues.

Table V-5 gives the numerical results.

Table V-5

\[ \text{C-H stretching vibration data} \]

<table>
<thead>
<tr>
<th>Substance</th>
<th>( \text{C-H} ) stretch frequency</th>
<th>Unidentified 3050 band</th>
</tr>
</thead>
<tbody>
<tr>
<td>A 3-Me-trans-hexene-3</td>
<td>3023 cm(^{-1})</td>
<td>3061 cm(^{-1})</td>
</tr>
<tr>
<td>B 3-Me-cis-hexene-3</td>
<td>3022 cm(^{-1})</td>
<td>3038 cm(^{-1})</td>
</tr>
<tr>
<td>C 3-Me-trans-pentene-2</td>
<td>3021 cm(^{-1})</td>
<td>3006 cm(^{-1})</td>
</tr>
<tr>
<td>D 3-Me-cis-pentene-2</td>
<td>3032 cm(^{-1})</td>
<td>3004 cm(^{-1})</td>
</tr>
<tr>
<td>E 3,4-dime-trans-pentene-2</td>
<td>3024 cm(^{-1})</td>
<td>3001 cm(^{-1})</td>
</tr>
<tr>
<td>F 2,4-dime-cis-pentene-2</td>
<td>3004 cm(^{-1})</td>
<td>3002 cm(^{-1})</td>
</tr>
<tr>
<td>G 3-Me-cis-hexene-2</td>
<td>3025 cm(^{-1})</td>
<td>3054 cm(^{-1})</td>
</tr>
</tbody>
</table>
VI. For a pair of cis and trans trisubstituted ethylenes the $=\text{C} - \text{H}$ stretching frequency is about 10 cm$^{-1}$ higher for the cis isomer.

**Secondary effects**

The CH$_3$ deformation frequencies near 1380 cm$^{-1}$ and 1440 cm$^{-1}$.

On several instances we noted that the intensity of the methyl deformation modes are very sensitive to coupling, electrical, and sterical effects. For the API trisubstituted ethylenes, the following correlations were found:

VII. The absolute intensity of the 1380 cm$^{-1}$ CH$_3$ deformation vibration of trisubstituted ethylenes of the type $R_1$(CH$_3$)C=CH$R_2$ is lowest for the cis isomer.

VIII. The absolute intensity of the combined CH$_2$/CH$_3$ deformation band near 1450 cm$^{-1}$ of trisubstituted ethylenes is highest for the cis isomer. Table V-6 demonstrates these rules.

**Table V-6**

<table>
<thead>
<tr>
<th>Substance</th>
<th>1380 cm$^{-1}$ band (10$^6$ absolute intensity (cm$^2$/molecule)) integrated between 1335 and 1410 cm$^{-1}$</th>
<th>1460-1480 cm$^{-1}$ band (10$^6$ absolute intensity (cm$^2$/molecule)) integrated between 1410 and 1510 cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A 3-Me-trans-hexene-3</td>
<td>9.7</td>
<td>26.1</td>
</tr>
<tr>
<td>B 3-Me-cis-hexene-3</td>
<td>9.3</td>
<td>27.0</td>
</tr>
<tr>
<td>C 3-Me-trans-pentene-2</td>
<td>10.4</td>
<td>23.4</td>
</tr>
<tr>
<td>D 3-Me-cis-pentene-2</td>
<td>9.5</td>
<td>20.3</td>
</tr>
<tr>
<td>E 2,4-di-Me-cis-pentene-2</td>
<td>12.2</td>
<td>23.5</td>
</tr>
<tr>
<td>F 2,4-di-Me-trans-pentene-2</td>
<td>11.8</td>
<td>24.5</td>
</tr>
<tr>
<td>G 3-Me-cis-hexene-2</td>
<td>9.9</td>
<td>23</td>
</tr>
</tbody>
</table>

These rules are of restricted value only. When it is assumed in case of the 1380 band, the intensity effect being caused in some way by the CH$_3$ group(s) directly connected to the C=C bond, it is clear that the number of these methyl groups (one or two) may effect the intensity difference, and secondly the intensity difference will be obscured by the absorption of other methyl groups if present in the molecule.

Rule VII requires even more restriction, as on addition to the precautions mentioned above, the absorption of the CH$_2$ groups and the possible sterical influence on their intensity must be considered as well. Only when it could be proved that both direction and amplitude of the sterical effect on the CH$_2$ intensity is either equal to that of the CH$_3$ groups or zero, the rule could be used with more confidence.
There is some indication for the latter possibility, as can be seen from Table V-6 third column. The sterical intensity effect amounts about $1 \times 10^{-8}$ absolute units for the pair $AB$ (having one CH$_3$ and two CH$_2$ groups directly attached to the C=C band) and approximately $2.5 \times 10^{-8}$ absolute units for the pairs CD (two CH$_3$ and one CH$_2$) and EF (two CH$_3$ groups).

**Absorption bands uniquely characteristic for the cis/trans $R_1HC=C(CH_3)R_2$ system**

Lecomte and Naves claim to find (an) absorption band(s) between 984 and 999 cm$^{-1}$ for the system trans H-C=C(CH$_3$)- which they attribute to a (C-H) deformation, a rule which they deduced from spectra of a number of jonones and irones.

We do not agree with their conclusions because their spectra of β-iron and 2$_4$-Me-β-jonon show also a band in the region mentioned, although these substances have only a tetra substituted and a (trans) 1,2 disubstituted ethylenic bond.

On mono-methylation of the H-C=C-H double band indeed a second band arises, a doublet then which is also found for a number of analogous α-jonons and α-irons (however their spectrum of neo-α-iron which has not the -CH=C(CH$_2$)-C=O structure also shows the doublet). It is therefore felt that one of the bands they observed is due to a C=C=CH$_3$ bending deformation (of the C=C double band of the ring system), explaining why it is also found in case of tetra substitution. The second one must be due to the -CH=C(CH$_3$)-C=O system, either to an analogous bending deformation, or indeed to an (in plane!) deformation of the one hydrogen atom.

There is certainly no possibility to decide which is which in case of an doublet and even more certain there is not a single reason why one of these bands should be characteristic for the trans HC=C-CH$_3$ system, because no spectra are given for the corresponding cis isomers, (if they would exist at all).

Turning to our spectra of the API substances, we indeed found absorption bands in the region mentioned, but no regular difference between cis and trans isomers could be decided to.

**V-3. The Nuclear Magnetic Resonance Spectra**

Of the two methods discussed in this Chapter, NMR spectroscopy is at first sight certainly the most promising for distinguishing cis-trans isomers. The peculiar properties of the C=C band lead to specific long-range effects across 4 or more chemical bonds. The chemical shifts as well as the coupling constants may provide suitable information for the distinguishing between two cis-trans isomers of the trisubstituted ethylene type. It may even be hoped that indications for an absolute assignment may be found,
which is important especially if only one of the isomers is available.

In Table V-7 the \( r \)-values of the one olefinic proton of six API samples are given (it must be noted that the 3-Me-hexenes-3 have been relabelled as already discussed in the infrared section of this Chapter. The experimental NMR results again justify this relabelling). The figures have been derived from the spectra given at the end of this section.

**Table V.7**

**VALUES OF OLEFINIC PROTON OF \( R_1R_2C=CHR_3 \) GROUPS**

<table>
<thead>
<tr>
<th>SUBSTANCE</th>
<th>( r )</th>
<th>( \Delta r ) observed</th>
<th>( \Delta r ) calculated by formula V-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-Me-pentene-3</td>
<td>4.57</td>
<td>-0.05</td>
<td>+0.03</td>
</tr>
<tr>
<td></td>
<td>4.54</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-Me-hexene-3</td>
<td>4.38</td>
<td>-0.00</td>
<td>+0.02</td>
</tr>
<tr>
<td></td>
<td>4.30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3,4-di-Me-pentene-3</td>
<td>4.88</td>
<td>-0.10</td>
<td>+0.07</td>
</tr>
<tr>
<td></td>
<td>4.70</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

From this table the following correlation can be derived:

IX. Within a pair of trisubstituted ethylenic cis-trans isomers, the olefinic proton of the cis isomer will have the higher \( r \) value (will be more shielded).

This phenomenon can be explained through sterical hindrance. In the infrared section of this Chapter it has already been argued, that sterical hindrance upsets the \( sp^2 \) hybridization at the \( C=C \) bond. The \( =C-H \) stretch frequency, for instance, was found to be higher for the cis isomer as a result of the increased \( s \) character of that \( =C-H \) bond. Now one of the main effects which determines the proton screening in NMR is the diamagnetic atomic screening of the hydrogen atom itself. This effect can be represented by Lamb's* formula:

\[
\sigma = \frac{e^2}{3mc^2} \int \frac{\lambda \psi_{1s}^2}{r} \, dr \quad \text{V-1}
\]

where \( \sigma \) is the screening constant and \( \lambda \) is the effective number of electrons in the hydrogen \( \psi_{1s} \) atomic orbital. So, from equation V-1 it is clear that an increased \( s \) character involves a more effective shielding (a higher \( r \)-value).

If one reads Table V-7 vertically, the increasing \( \Delta r_{1c} \) can be explained by this hypothesis, because the bulkiness of the hindering substituents increases in the same direction (ethyl-methyl, ethyl-ethyl and isopropyl-methyl are the interacting groups respectively). If sterical hindrance were the only effect, the \( r \) value for trans-3-Me-pentene-2 and trans-3,4-di Me-pentene-2 would
be identical, since in both molecules $R_2$ and $R_3$ are CH$_3$ groups.

The experimental values are 4.84 and 4.75 however. Any paramagnetic contribution of the hydrogen atom itself can be ignored, because of the absence of low-lying hydrogen p orbitals. Thus, the origin of the just mentioned effect can only be sought in the magnetic anisotropy of neighbouring electron groups. Especially the anisotropy of the C-C single bond, which is approximately equal to $-5.5 \times 10^{-30}$ cm$^3$/molecule might be responsible for the effects observed. This kind of paramagnetic shielding may be represented by McConnell’s formula:

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

Here $r$ stands for the distance between the gravity centre ($G$) of the anisotropic electron group and the screened proton, and $\theta$ is the acute angle between the symmetry axis of the (axially symmetrical) electron group and the direction of $r$. $X_{//} - X_\perp$ is the diamagnetic anisotropy. For $\theta < 55.44^\circ$ a negative $\sigma_{\text{av}}$ will be found. Using formula V-2 it appears that the olefinic proton of trans-3,4-di Me-pentene would be 0.03 ppm more deshielded (0.03 lower $r$ value) than the trans-3-Me-pentene-2. This is the correct sign, but the actual difference is somewhat larger (0.09 ppm).

It will be investigated now, whether the C-C bond anisotropy theory would be able to explain sign and magnitude of the $\Delta r_{1c}$ values of Table V-7.

![Diagram](attachment:image.png)

Cis-3-Me-hexene-3 has one $\beta,\gamma$ C-C single bond more in the position trans to the olefinic proton, and one $\beta,\gamma$ C-C single bond less in the cis position as compared to trans-3-Me-hexene-3. As the trans deshielding is somewhat larger than the cis deshielding, $\Delta r_{1c} = +0.03$ is calculated!
So, even the sign of the calculated $\Delta r_{\text{c}}$ is not in agreement with the experimental results. This leads to the conclusion that the C–C single bond anisotropy effect counteracts the sterical hindrance effect, while the latter is always the predominating effect.

The $r$ values of the proton-containing substituents of the $R_1R_2C=CHR_3$ group have also been measured. Little information, however, could be gained, except for two points worth mentioning:

The CH$_3$ substituent in trans-3-Me-hexene-3 absorbs at $r = 8.44$, while at the cis isomer $r = 8.35$ is found. The sign of this effect is in agreement with the sign predicted from the carbon-carbon single bond anisotropy theory, although from formula $V-2$ a $\Delta r_{\text{c}} = +0.35$ can be calculated. This is once more a proof for the correctness of our cis-trans relabelling of these two substances. Furthermore, on this finding the assignment of the two methyl signals of the isopropylidene group has been based (see Table IV-4). The other remarkable point is the large $\Delta r$ observed for the methine proton of cis- and trans-3,4-di Me-pentene-2, ($r = 7.17$ and $r = 7.76$ respectively). We have no adequate explanation for this large effect.

The long-range coupling across a C=C bond

Spin-spin interaction is a powerful tool in structural analysis. Generally speaking, it reveals to what neighbours a certain group is bonded. As a rule spin-spin coupling extends over no more than 3 chemical bonds. For instance, the coupling between the two proton groups of $-\text{CH}_2-\text{CH}_3$ (3 chemical bonds) amounts to 7-8 cps. If a C=C bond is involved, the coupling constants may increase considerably. Coupling constants up to 19 cps have been reported for the olefinic protons of trans-1,2-disubstituted ethylenes. The analogous cis isomers always show a $J_{\text{cis}}$ for the two olefinic protons, which is very nearly half the value of $J_{\text{trans}}$. The $J_{\text{trans}}/J_{\text{cis}} = 2$ ratio also resulted from the theoretical calculations made by Karplus$^*$. In trisubstituted ethylenes only one olefinic proton is present, but in many spectra it is found that, apart from the primary spin-spin coupling $J'$, the olefinic proton signals show further fine structure
This now can be ascribed to long-range coupling across the double bond, the spin-spin interaction now extending over four chemical bonds.

Based on Karplus calculations, it is furthermore assumed that \( J'' \) (also named trans- or secondary spin-spin coupling) will always be larger than \( J''' \) (cis- or tertiary coupling), although no longer a ratio \( J''/J''' = 2 \) can be expected. Of course, \( J'' \) and \( J''' \) are very small; they are found to vary between 0.3-2.0 cps. (As spin-spin coupling is a reciprocal process, similar fine splitting must be expected on the signals of the two alkyl proton groups involved as well). The olefinic proton fine structure of trans-3-Me-hexene-3, for instance, can be understood by assuming \( J'' = 1.6 \text{ cps} \) (with quartet multiplicity) and \( J''' \approx 1.2 \text{ cps} \) (triplet multiplicity).

As the quartet multiplet has the higher coupling constant, it is concluded that a CH\(_3\) group is in a trans position relative to the olefinic proton. (n equivalent nuclei give an n+1 multiplicity on the nuclei to which it is coupled).

The spectrum (figure V-5) shows that the quartet fine structure is very definite, and one might be tempted to assume \( J'' = 1.50 \) and \( J''' < 0.3 \text{ cps} \). In the latter case, however, the presence of lines no. 6 and no. 11 cannot be explained. The way in which such a fine structure analysis is carried out is more or less by trial and error. One starts with good guesses for \( J'' \) and the two multiplicities to be expected, and then tries several values of \( J''' \), until one which corresponds well with the experimental spectrum is found. Usually, two possibilities for \( J''' \) are found (like the values 1.2 and 0.3 for trans-3-Me-hexene-3, just mentioned), but this does not influence the final conclusions. In unfavourable cases, \( J''/J''' \) may be such that no separated lines can be observed and consequently an analysis is impossible. If, on the other hand, good multiplets are observed, the effect of the larger \( J'' \) will always predominate in the pattern. It was also observed that cis isomers are more reluctant to give fine-structure on the olefinic proton than the trans isomers. This is probably caused by a paramagnetic line-broadening, as it is known that cis isomers are inclined to form oxygen complexes. Although all the samples were vacuum distilled, the complete removal of any trace of oxygen is not easily achieved.

Nevertheless, we postulate the important rule;

X. The absolute configuration of cis- or trans trisubstituted ethylenes can be derived from the fine-structure which appears on the signal of the olefinic proton.

Assuming that the trans long-range coupling constant \( J'' \) is always larger than the cis long-range coupling constant \( J''' \), the multiplicity caused by \( J'' \) immediately gives the number of hydrogen atoms on the \( C_β \) atom of the substituent trans to the olefinic proton.
Whether rule X can be applied depends on the following conditions:

1. The instrument must be capable of resolving (at least partially) separations of 0.4 cps;

2. The sample must be oxygen-free to a high extent, to avoid line-broadening;

3. One needs some luck as to the $\frac{J''}{J'''}$ ratio. $J''$ (quartet) /$J'''$ (triplet) 1.5 for instance, will not give any measurable fine-structure;

4. The rule will not apply, if the numbers of hydrogen atoms on each of the $C\beta$ atoms of $R_1$ and $R_2$ (of the general $R_1R_2C=CHR_3$ structure) are the same.

Of course, the long-range coupling effect must also be found on the alkyl substituent signals. Complex primary coupling by small $\Delta\nu/J'$ ratios in many cases complicate the spin-spin multiplets. Even if the substituent is a methyl group, the spectrum is more complicated as would be anticipated. The methyl signal of trans-3-Me-hexene-3 (see fig. V-7) would be expected to consist of 6 lines (doublet by $J''$ and triplet multiplicity by $J'''$). In fact, at least 10 lines were observed. This could be explained by the existence of a longe-range coupling effect to the "gem" -CH group.

In the figures V-2 to V-8 it has been tried to sketch the analysis of the long-range coupling multiplets, wherever feasible.

Finally, the possibility of spin-spin decoupling by double resonance techniques should be mentioned. By this method, either the $J''$ of the $J'''$ coupling effect can be annihilated, by irradiation at suitable frequencies. This would simplify the spectra considerably. The above mentioned conditions 1, 2 and 3 would be much less stringent, and the interpretation of the spectra would be easier and more straightforward.

Recapitulating, it may be concluded that NMR spectroscopy provides means to establish the cis- or trans configuration of trisubstituted ethylenes.
FIGURE V-2

TRANS-3-ME-HExENE-3

FIGURE V-3

CIS-3-ME-HexENE-3
Figure V.7

CI-3,4-DIMETHYL-PENTENE-2

Figure V.9

TRANS-3,4-DIMETHYL-PENTENE-2
VI-1. The cis-trans isomerism of the neryl and geranyl structures

It is generally accepted that nerol has the cis-3,7-di-Me-2,6-octadienol-1 structure, and that geraniol is the corresponding trans-isomer.

\[
\begin{align*}
\text{Neryl} & : \quad \begin{array}{c}
\text{CH}_3 \\
\text{H}_2\text{C} \\
\text{H}_2\text{C} \\
\text{CH} \\
\text{CH}_2\text{O} \\
\text{CH}_3 \\
\text{CH}_3
\end{array} \\
\text{Geranyl} & : \quad \begin{array}{c}
\text{CH}_3 \\
\text{H}_2\text{C} \\
\text{H}_2\text{C} \\
\text{CH} \\
\text{CH}_2\text{O} \\
\text{CH}_3 \\
\text{CH}_3
\end{array}
\end{align*}
\]

Literature investigation showed, however, that this assignment has been based mainly on one observation: Zeitschel\(^a\) has reported that on dehydration with diluted sulfuric acid, nerol and geraniol both form \(\alpha\)-terpinolene (1-Me-4-isopropyl-cyclohexene-1), but that the reaction rate for nerol is much higher. This seems to be a good argument, but further evidence is desired.

In Table III-2 some physical constants are given of our own, highly purified, nerol and geraniol samples (and their acetates). It may be added here that Simonsen\(^b\) quotes 225-226°C b.p. for nerol and 229-230°C b.p. for geraniol. Boiling point and retention indices are lower for nerol (and derivatives), thus supporting the cis-assignment. Densities and refractive indices, however,
indicate the reverse assignment. It is geraniol which has the higher density and refractive index. In our opinion, the density argument is better than a boiling point argument, but still further evidence is needed. It was therefore tried to apply the rules, developed in the preceding Chapter. Most of these rules cannot be used, because a second trisubstituted ethylene group, present in the molecule, overlaps most of the absorptions of interest.

Only the application of rules 1, 2, 3, 9 and 10 may be tried, but even with these rules serious interactions of the isopropylidene group should be reckoned with.

Number of infrared peaks in the 2-15 μ region.

Although the IR spectra of nerol and geraniol are very similar, nerol shows two bands, at 1146 and 1038 cm\(^{-1}\) which are absent in geraniol. The presence of a band near 1160 cm\(^{-1}\) in the IR spectrum of geraniol is questionable. Nerylacetate has (weak) bands at 1150, 1112 and 1090 cm\(^{-1}\), which are absent in the spectrum of geranylacate, while the latter has only one band at 1109 cm\(^{-1}\), which is absent in the spectrum of nerylacetate. Therefore, rule I of Chapter V, which states that the cis isomer will have the larger number of peaks, indicates the cis structure for nerol.

The C=C stretching frequencies are found at 1671 cm\(^{-1}\) for nerol and 1673 cm\(^{-1}\) for geraniol, while for their respective acetates 1668 and 1672 cm\(^{-1}\) was found. When rule II of Chapter V is applied, which states that the cis isomer will have the lower C=C stretching frequency, again the cis structure for nerol is indicated.

An investigation of the intensities of the C=C stretching frequencies led to the same conclusion. For the extinction coefficients \(\epsilon'\) and the halfwidths \(\Delta \nu_{1/2}\), the following figures were found: Nerol \(\epsilon' = 21, \Delta \nu_{1/2} = 27\) cm\(^{-1}\), Geraniol \(\epsilon' = 24, \Delta \nu_{1/2} = 34\) cm\(^{-1}\), Nerylacetate \(\epsilon' = 26, \Delta \nu_{1/2} = 28\) cm\(^{-1}\), Geranyl acetate \(\epsilon' = 28, \Delta \nu_{1/2} = 31\) cm\(^{-1}\), i.e., both extinction and intensity are smaller for the neryl derivatives. Rule III, which predicts a lower intensity and extinction for the cis isomer, indicates that nerol has this cis structure. It may be mentioned here that the C=C stretching could be studied, only because the extinction coefficient of the \(R_1 R_2 C=CH-CH_2-O\) group in question is about 8 times larger than the extinction coefficient of the other \(R_1 R_2 C=CHR_3\) group, which is also present in the molecule (see also Chapter IV on this subject).

The \(\tau\) value of the olefinic proton of the \(C=CH-CH_2-O\) group in which we are interested only, is somewhat lower than the \(\tau\) value of the isopropylidene group. In order to get an improved accuracy, each spectrum was run 8 times.
The results are as follows:

\[
\begin{align*}
\text{Nerol} & \quad r = 4.646 \pm 0.002 \quad \Delta r = + 0.012 \\
\text{Geraniol} & \quad r = 4.634 \pm 0.004 \\
\text{Neryl acetate} & \quad r = 4.679 \pm 0.004 \quad \Delta r = - 0.009 \\
\text{Geranyl acetate} & \quad r = 4.688 \pm 0.003
\end{align*}
\]

The \( \Delta r \) values are very small (about 0.01 in \( r \) value) while a \( \Delta r_{tc} \) of about 0.1 was anticipated (see Table V-8). In fact, the differences are hardly larger than the sum of the standard deviations; the values measured overlap to some extent. Furthermore, systematic errors, such as caused by the uncertainty in the position of the centre of absorption will be involved as well.

The small \( \Delta r_{tc} \) values support the hypothesis (see Chapter V), that two counteracting effects occur at the same time.

The sterical hindrance, which results in a negative \( \Delta r_{tc} \) value (see Chapter V), is certainly not less than in the case of the two 3-Me-hexenes-3, but the influence of the anisotropy of the C-C bonds may be much larger. In the two hexenes, the cis-trans difference lies in the interchange of a methyl and an ethyl group, and the anisotropy effect was calculated to be \( \Delta r_{tc} = + 0.03 \).

In nerol and geraniol a methyl and a \( \text{CH}_2-\text{CH}_2-\text{CH}=\text{C}(\text{CH}_3)_2 \) group are interchanged, which will lead to a much higher anisotropy effect, and this may just neutralize the sterical hindrance effect, resulting in a nearly zero \( \Delta r \) value. The acetates will however differ from their alcohols only as to sterical hindrance, so at any rate, for the acetates the \( \Delta r \) (trans minus cis) must be lower than for the alcohols. It was found that \( \Delta r \) (neryl minus geranyl) was about 0.02 \( r \) lower for the acetates than for the alcohols. Thus it might be concluded that neryl has the trans structure.

In this reasoning it has been assumed that the average position of the acetate C=O group, relative to the olefinic proton, is the same for both cis and trans structure. However, sterical hindrance may result in different average C=O positions (relative to the olefinic proton). The anisotropy of the C=O bond may then have an effect on the shielding of the olefinic proton, which is non-identical for the cis and trans acetate. With this possible complication in mind, the conclusion that the \( r \) values of the olefinic proton would indicate a trans structure for nerol (rule IX Chapter V), should be considered with some reserve.

After that, a study of the long-range fine structure on the olefinic proton NMR signal (rule X Chapter V) was made. Unluckily enough, no well separated fine structure could be measured, neither for the two alcohols nor for their esters. This in spite of the fact that at the time of measurement
we had a field homogeneity of $6.5 \times 10^9$. Furthermore the shapes of the olefinic proton signals of the isomers were very much alike. This is an example of "bad luck" one may encounter (see also Chapter V; "Conditions for the observation of long-range coupling"). After ample considerations it was found that the fine structures resolved, fit in better with a trans structure for nerol and a cis structure for geraniol, than with the reverse assignment. Here too, this conclusion is not very stringent.

The final result is that chemical evidence, boiling point, retention indices and three infrared correlations are in agreement with the cis structure for nerol, while density, refractive index and the two NMR correlations point to the trans structure.

The NMR conclusions are not very reliable but it may be expected that in due time proton-proton decoupling experiments will provide the final answer (see, however, also section II-3 for an alternative suggested proof).

VI-2. The cis-trans isomerism of the allo ocimenes

O'Conner and Goldblatt seem to be first who produced the two allo ocimene isomers in a more or less purified state. The following physical data have been derived from their paper:

<table>
<thead>
<tr>
<th></th>
<th>b.p.</th>
<th>$\varepsilon^2$</th>
<th>$d^{20}$</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\varepsilon_{\text{max}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(4-trans, 6(7)-cis) allo ocimene</td>
<td>91</td>
<td>1.5446</td>
<td>0.0118</td>
<td>265</td>
<td>39,900</td>
</tr>
<tr>
<td>(4-trans, 6(7)-trans) allo ocimene</td>
<td>99</td>
<td>1.5446</td>
<td>0.0060</td>
<td>270</td>
<td>31,500</td>
</tr>
<tr>
<td>(4-trans, 6(7)-trans) allo ocimene</td>
<td></td>
<td></td>
<td></td>
<td>276</td>
<td>32,900</td>
</tr>
<tr>
<td>(4-trans, 6(7)-trans) allo ocimene</td>
<td></td>
<td></td>
<td></td>
<td>289</td>
<td>33,600</td>
</tr>
</tbody>
</table>
The authors do not mention how they did arrive at the assignment given above. Probably they were guided mainly by the U.V. wavelengths of maximum absorption ($\lambda_{max}$). They also gave infrared spectra, the quality of which was insufficient for the applications of the rules developed in Chapter V.

Klouwen and ter Heide* have given the reverse assignment, based on GLC retention data only.

It was felt, therefore, that further evidence was desired. Unfortunately, however, the purification of the two isomers with preparative-scale GLC proved to be very difficult if not impossible. It could be shown that the two isomers convert themselves into each other. At the temperature (140°C) prevailing in the gaschromatograph the conversion rate is such that, combined with the long residence time of about 3 hours, it becomes impossible to obtain the two isomers in a substantially pure state. A small amount of 80% pure allo ocimene I (the lower boiling isomer), as well as a small amount of 95% pure allo ocimene II (the higher boiling isomer) could however be isolated after several repeated separations. Neither the quantities, nor the purities in which they were obtained, allowed for useful NMR spectra. Only improved IR spectra could be made.

In figure VI-1 the NMR spectrum of the starting material (90% isomer mixture research sample, gratefully received from Hercules Powder Cy), has been given. This spectrum is of some interest as it proves unambiguously that the allo ocimenes have only olefinic protons and methylprotons of CH$_3$ groups directly connected to a C=C bond, in a ratio 1:3. This is direct evidence for the assumed overall structure, which before was based on chemical evidence only.

In figures VI-2 and VI-3 the IR spectra of the two allo ocimenes are given. Peaks, probably due to impurities (in fact only the other isomer), have been marked I or II.

The overall IR spectra are in agreement with the assumed structure for allo ocimene. Absorptions near 3040 cm$^{-1}$ indicate the presence of =C-H olefinic protons. The absorptions near 1650, 1630 and 1590 cm$^{-1}$ indicate a system of two or three conjugated C=C bonds. The out-of-plane deformation range is rather complex. The investigation of a number of published spectra showed that the o.o.p. deformation frequency of a trisubstituted ethylenic group is much lowered if it is conjugated to a symmetrically disubstituted double bond. Frequencies of $\nu = 806$ cm$^{-1}$ (Sadtler 12,966), $\nu = 817$ cm$^{-1}$ (API 1183) and $\nu = 798$ cm$^{-1}$ (DMS 1859) may be quoted. Therefore the strong vibration observed somewhat below 800 cm$^{-1}$ is assigned to the o.o.p. deformation of the hydrogen atom on the C$_7$ place. The o.o.p. deformation of the hydrogen atoms on C$_1$, C$_4$ and C$_3$ will be strongly coupled; the strong
absorptions at 1025, 985, 953, 874 and 839 cm⁻¹ are therefore assigned to this group.
It will be tried now to apply some of the rules developed in Chapter V.

Number of peaks
Allo ocimene I shows peaks near 1290, 1239, 1087, 1035 and 785 cm⁻¹, which are absent in the spectrum of the allo-ocimene II, while the latter shows peaks near 1352, 1908 and 794 cm⁻¹ which are absent in the spectrum of allo ocimene I. Using rule I of Chapter V ("The cis isomer has the larger number of peaks"), the cis structure for allo ocimene I (low b.p.) is indicated

The C=C stretching frequency
The stretching frequencies found for allo ocimene I are 1649, 1630 (sh) and 1585 cm⁻¹, while for allo ocimene II, these vibrations are found at 1650, 1630 and 1595 cm⁻¹.
Application of rule II of Chapter V ("The cis isomer has the lower C=C stretching frequency"), points again to the cis structure for allo ocimene I.
CHAPTER VI

The out-of-plane deformation near 800 cm\(^{-1}\)
Allo ocimene I shows this vibration at 785 cm\(^{-1}\) (\(\epsilon' = 65\)), while allo ocimene II shows a similar band at 795 cm\(^{-1}\) (\(\epsilon' = 90\)).

On the application of rules IV and V of Chapter V ("The cis isomer has the lower frequency and the lower intensity for the o.o.p. deformation") the cis structure of allo ocimene I is again twice indicated.

From the foregoing discussion it may be concluded that the (low boiling) allo ocimene I has the 6(7)-cis structure, while the (higher boiling) allo ocimene II has the corresponding 6(7)-trans structure.

VI-3. 3,7-di-Me-octene-1

\[
\begin{align*}
\text{CH}_3 & \\
\text{CH} & \\
\text{H}_2\text{C} & \quad \text{CH} \\
\text{H}_2\text{C} & \quad \text{CH}_2 \\
\text{CH} & \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}
\]

This substance was obtained from the pyrolysis of tetrahydrogeranyl acetate at 440°C (see Chapter III for a description of the macro pyrolysis apparatus). The compound was purified by preparative-scale GLC. After having injected three times 1.5 ml pyrolysis product, 600 \(\mu\)l of the pure material could be collected. An analytical GLC analysis proved that the substance was pure for at least 99.5\%.

Probably, the substance has previously been made by Smith and Raoult\(^*\) who, by pyrolysis at 360° of tetrahydrogeranyl stearate, obtained a product with b.p. 152°C, which was not further purified. Longinow and Margolis\(^*\) describe a product obtained from 2,6-di-Me-octane-1-bromide plus chinoline. They quote 154°C b.p., \(d_4^{20} = 0.7396\) and \(n_D^{20} = 1.4212\). Our product has \(n_D^{25} = 1.4144(3)\). If we take \(\Delta n/\Delta t = -0.0005\) per \(^\circ\)C, the estimated \(n_D^{29}\) of our product is 1.4169; still much less than the value quoted by Longinow and Margolis.

It may be said therefore, that it is not likely that this compound has previously been obtained in a substantially pure state. Infrared and NMR spectra
FIGURE VI-2
ALLO OCIMENE I (4-TRANS, 6(7) CIS, ALLO OCIMENE), 80% PURE

FIGURE VI-3
ALLO OCIMENE II (4 TRANS, 6(7) TRANS, ALLO OCIMENE) 95% PURE
proven unambiguously the assumed structure (see below). One other figure may be mentioned: the Ultra Violet spectrum showed an absorption, the maximum of which was below 186 nm. The extinction coefficient (measured in n-heptane) at 190 nm was \( \epsilon_{190} = 4700 \), while the absorption at 200 nm was about 10 times less. This is sufficient evidence for the presence of one C=C bond of the monosubstituted vinyl type.

From the infrared spectrum the following conclusions could be derived (see also figure VI-4).

a. \( a = CH_2 \) stretching frequency at 1645 cm\(^{-1}\) (\( \epsilon' = 34 \)), \( a = CH_2 \) deformation frequency at 1418 cm\(^{-1}\) and out-of-plane deformations at 990 cm\(^{-1}\) (\( \epsilon' = 57 \)) and 906 cm\(^{-1}\) (\( \epsilon' = 161 \)) prove the existence of one HC=CH\(_2\) vinyl group.

b. Both CH\(_2\) and CH\(_3\) groups are present (C-H stretchings between 2800 and 3000 cm\(^{-1}\) as well as the deformation modes of CH\(_2\) and CH\(_3\) in the 1350-1500 cm\(^{-1}\) region). The shape of the 1360-1390 cm\(^{-1}\) band revealed the presence of at least one C-(CH\(_3\))\(_2\) and one other CH\(_3\) group. Integration from 1335-1400 cm\(^{-1}\) gave an absolute intensity of A = 12.7 cm\(^2\)/molecule/sec, which corresponds with 3 or 4 methylgroups (From Table IV-6 we calculated A = 11.1 cm\(^2\)/molecule/sec for 3 methylgroups).

The absolute intensity of the 1430-1510 cm\(^{-1}\) region is A = 23.3 cm\(^2\)/molecule/sec, after subtraction of the contribution of the three CH\(_2\) groups (being 3 \( \times \) 5.2 = 15.6 cm\(^2\)/molecule/sec), 7.7 cm\(^2\)/molecule/sec is left, which would indicate 7.7/1.7 = 4.5 CH\(_2\) groups. This number is not very reliable, as it results from a subtraction of two large numbers.

c. The absorption in the 720-750 cm\(^{-1}\) region (a single sharp band at 728 cm\(^{-1}\)) indicates the presence of a chain of 3 or 4 CH\(_2\) groups. In combination with b it follows that probably all the CH\(_2\) groups of the molecule form one chain -(CH\(_2\))\(_3\) or -(CH\(_2\))\(_4\).

From the NMR spectrum (figure VI-5) the following conclusions were derived:

a. The molecule contains one vinyl group. The complex pattern in the 3.5 to 5.5 \( \tau \) region could be analyzed completely. The splitting of the original four lines of the H\(^2\) signal into eight lines (coupling constant about 6.6 cps) proves that the substituent of the vinyl group contains one hydrogen atom on its first carbon atom, (>CH-CH=CH\(_2\)).

b. The broad line near \( \tau = 8.7 \) is due to the nearly equivalent CH\(_2\) groups none of which is connected either to a C=C group, or to a CH\(_3\) group.
Figure vi-4
3.7-Di-Me-octene-1

Figure vi-5
3.7-Dimethyl-octene-1
c. The 8.9-9.3 r-region proves the presence of three CH₃ groups.
     The doublet with the lower intensity and the lower r value (r = 8.95) 
     is assigned to a CH₃-CH-C≡C group. The doublet with J = 6.2 cps arises 
     from coupling with a methine proton.
     The other, much stronger doublet, which has a r = 9.06 is assigned to a 
     -CH-(CH₃)₂, group.
     The combination of these conclusions led unambiguously to the 3,7-di- 
     Me-octene-1 structure suggested.

VI-4. Δ⁴(⁸) p-menthene

We have made this compound rather unintentionally and unexpectedly. In 
analogy to the preparation of 3,7-dimethyl-octene-1 by the pyrolysis of 
tetrahydrogeranyl acetate, we tried to prepare 3,7-dimethyl-1,6-octadiene 
by pyrolysis of citronellyl acetate. The chromatogram of the pyrolysis-
products (see section II-3) showed a somewhat complex pattern. The main 
product was then isolated by preparative scale GLC. From each injection of 
3 ml crude pyrolysis product 500 µl material of 90% purity could be collec-
ted. When this product was reinjected no further increase in purity could be 
achieved, as a result of thermal rearrangement in the gaschromatograph. 
From the 90% pure material (containing two impurities of about 5% each) 
UV, IR and NMR spectra were made (see figures VI-6 and VI-7). The UV 
spectrum showed a well resolved maximum (in n-hexane) at 196.7 nm with 
a molecular extinction coefficient of εₘ₉₉ = 8040. This is direct evidence 
for one C=C double bond of the tri- of tetra substituted type. This proved 
already that ring closure had occured, as otherwise two C=C bonds would 
have been found. From the simple UV spectrum only, it was concluded that 
either Δ⁴⁻, Δ³⁻ or Δ⁴(⁸) p-methene had been formed.
The NMR spectrum (figure VI-6) provided evidence for the tetra substituted ethylenic structure.

Near $r = 5.3$ only a very small olefinic proton signal, corresponding with 5-10% impurity at most, was found. A strong signal at $r = 8.41$ revealed however the presence of two $\text{CH}_3$ groups connected to a $\text{C}=\text{C}$ bond, while from a somewhat broader signal around $r = 7.9$, the presence of two $\text{CH}_2$ groups connected to a $\text{C}=\text{C}$ bond was concluded. This proves the presence of a $(\text{CH}_2)_2\text{C}=\text{C}(\text{CH}_3)_2$ group.

Furthermore, the signal in the $r = 8.8-9.2$ region forms evidence for at least one $\text{C}-\text{C}-\text{CH}_3$ group and one or more $\text{C}-\text{C}-\text{CH}_2-\text{C}-\text{C}$ groups. A first glance at the IR spectrum shows the $R_1R_2\text{C}=\text{CH}_2$ group; $\nu = 1645$ cm$^{-1}$ ($\epsilon' = 4$) and $\nu = 882$ cm$^{-1}$ ($\epsilon' = 14$), but the extinction coefficients are much too low. (Also the small $r = 5.3$ signal of the NMR spectrum points to a $R_1R_2\text{C}=\text{CH}_2$ structure). This impurity is most probably the $\Delta^8$ $\text{p}$-menthene. The single 1372 cm$^{-1}$ $\text{CH}_3$ deformation band proves the absence of a $\text{CH}-(\text{CH}_3)_2$ group (this group has a doublet in this region). The integrated 1330-1410 cm$^{-1}$ region indicated the presence of 3.3 methyl groups, while from the 1410-1510 cm$^{-1}$ band the presence of 3 to 5 $\text{CH}_2$ groups could be calculated.

Absorptions at 1187, 1150 and 857 cm$^{-1}$ indicate the $\text{C}(\text{CH}_3)_2$ structure. As there is no isopropylgroup (no doublet near 1380 cm$^{-1}$) this points to an $=\text{C}(\text{CH}_3)_2$ group. Methyl group connected to $\text{C}=\text{C}$ bond is more directly proved by the 1080-1095 cm$^{-1}$ band.

Finally a medium band at 1247 cm$^{-1}$ may be mentioned as it may point to a cyclohexane or cyclohexene ring in the main component.

Both NMR and IR spectrum are in complete agreement with the assumed $\Delta^8$ $\text{p}$-menthene structure.

The compound is probably identical to that prepared by Semmler and Feldstein* who isolated a hydrocarbon from pulegon hydrazone plus sodium ethoxide. Frank and Berry* also claim that they prepared the compound without giving any explicit structural proof. The infrared spectrum which they published is, however, in general agreement with our findings.
FIGURE VI-6
$\Delta^4(8)$ P-MENTHENE

FIGURE VI-7
$\Delta^4(8)$ P-MENTHENE

Impurity (3%)
Impurity (5%)
CHAPTER VII

EXPERIMENTAL DETAILS ABOUT THE SPECTROMETRICAL MEASUREMENTS

VII-1. Optimum experimental conditions for infrared intensity measurements

In infrared spectroscopy absolute intensities are usually to be preferred rather than molecular extinction coefficients. The latter vary very much due to external effects (like concentration, solvent and pressure), internal effects (like sterical hindrance) and instrumental effects (insufficient resolving power).

Absolute intensities appear to be far less dependent on these effects, and when they vary, the differences can be turned into correlations of analytical importance as has been done in the Chapters IV and V.

Special attention was paid to the accuracy with which intensities can be measured. All absorption spectrometers measure the transmission $T$ ($T = I/I_0$). The accidental error in $T$, $\Delta T$, may be considered a constant, independent of $T$, and determined only by the noise of the light source, detector, amplifier and recorder.

Since the extinction is defined by

$$E = -10 \log T,$$

VII-1

after differentiation, it follows that

$$\frac{\Delta E}{E} = 0.434 \frac{10^E}{E} \cdot \Delta T$$

VII-2

This error function has a minimum for $E = 0.434$ with a minimum value of $(\Delta E/E)_{\text{min}} = 2.71 \times \Delta T$. 

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So, the relative extinction accuracy is at least 2.71 times less than the transmission accuracy.

When an absorption band is integrated, the inaccuracy will be even greater, because at most two points will have the optimum E value. We will now try to estimate the relative error in integrated intensities. We shall distinguish two cases; the absorption band may be or may be not of Lorentzian shape.

1. The absorption band is purely Lorentzian.

A Lorentzian shape is defined by

\[ E_\nu = \frac{E_0 b^2}{(\nu - \nu_0)^2 + b^2} \] 

the area of which is given by

\[ A = \pi \int_{-\infty}^{+\infty} E_\nu d\nu = \pi E_0 b, \] 

so that only \( E_0 \) and \( b \) need be measured.

Accordingly, the error in \( A \) will be given by

\[ \frac{\Delta A}{A} = \sqrt{\left(\frac{\Delta E_0}{E_0}\right)^2 + \left(\frac{\Delta b}{b}\right)^2} \]

of which \( \Delta E_0 / E \) is already given by equation VII-2.
\( \Delta b / b \) depends on \( \Delta E_0 \) and on the linewidth and frequency-scale expansion of the absorption band recorded.
Suppose the linewidth of the pen trace is equal to $\Delta d$; this will introduce an uncertainty $\Delta b$ given by: 

$$\Delta b = \Delta d \csc \alpha.$$ (See sketch A).

Furthermore, if $E_0$ is measured with an error $\Delta E_0$, the height on which $b$ has to be measured has an uncertainty of $\frac{1}{2} \Delta E_0$, leading to another error in $b$ given by: 

$$\Delta b = \frac{1}{2} \Delta E_0 \cot \alpha.$$ (See sketch B).

Consequently, the total error in $b$ may be represented by

$$\left( \frac{\Delta b}{b} \right)^2 = \frac{1}{b^2} \left( \Delta d^2 \csc^2 \alpha + \frac{\Delta E_0^2 \cot^2 \alpha}{4} \right)$$

$\alpha$ can be eliminated by considering that

$$\tan \alpha = \left( \frac{dE}{d\nu} \right) E = \frac{E_0}{2b}.$$
leading to
\[
\left( \frac{\Delta b}{b} \right)^2 = \left( \frac{\Delta E_o}{E_o} \right)^2 + \frac{(E_o^2 + 4b^2)}{E_o^2 b^2} \cdot \Delta d^2
\]

Combining this with VII-5, the error in \( A \) will be
\[
\frac{\Delta A}{A} = \sqrt{2 \left( \frac{\Delta E_o}{E_o} \right)^2 + \frac{E_o^2 + 4b^2}{E_o^2 b^2} \cdot \Delta d^2}
\]

In order to make the term containing \( \Delta d \) of VII-7 neglectably small, we have the condition
\[
\Delta d^2 \frac{(E_o^2 + 4b^2)}{E_o^2 b^2} \ll 2 \left( \frac{\Delta E_o}{E_o} \right)^2
\]

For \( b = E_o \) (in length units on the recorder chart!) this reduces to
\[
\Delta d \ll \frac{2}{5} \Delta E_o^2
\]

Now for \( E_o = 0.43 \), \( \Delta T = 1\% \) and a recorder chart of 25 cm width, \( \Delta E_o \) will be 4 mm. Consequently, the effect of trace width on the accuracy of \( A \) will vanish, provided that the halfwidth of the recorded band will be equal or larger than the height of the band (both measured in length units on the chart) and provided that the pen trace width will be much smaller than 6 mm.

Under these conditions the error in \( A \) will be
\[
\frac{\Delta A}{A} = \frac{\Delta E_o}{E_o} \cdot \sqrt{2}
\]

or, if \( E_o = 0.434 \) (the optimum value), \( \Delta A/A = 2.71 \times 1.41 \). \( \Delta T = 3.8 \Delta T \).

This means that for an instrument with ± 1% transmission accuracy, the standard deviation for an integrated absorption band (when repeatedly measured) will be not better than about ± 1%. For a single measurement, the error may be as large as ± 10%, even if the optimum \( E_o \) value (\( E_o = 0.434 \)) and a much expanded frequency scale are chosen.
2. In case the absorption band is not Lorentzian — and in fact they hardly ever are — the absorption band must be integrated with a planimeter. It will be clear that, if we now integrate from $+\infty$ to $-\infty$, the relative error in $A$ will be infinitely large. Consequently, we have to choose integration limits, and therefore the relative error in $A$ will depend on this integration range.

The error in $A$ will be equal to

$$\frac{\Delta A}{A} = \frac{+a \int E_{\nu} \cdot d\nu}{-a \int E_{\nu} \cdot d\nu}$$

If equations VII-2 and VII-3 are used (for this error calculation we may assume that the band shape is still Lorentzian in a first approximation), VII-9 becomes

$$\frac{\Delta A}{A} = \frac{+a \int 0.434 \Delta T \exp \left[ E_0 b^2 / 0.434 \left[ (\nu - \nu_0)^2 + b^2 \right] \right] \cdot d\nu}{-a \int E_0 b^2 / [(\nu - \nu_0)^2 + b^2] \cdot d\nu}$$

This function was calculated for $E_0 = 0.1, 0.2, \ldots, 2.0$ and for the relative integration limits $a = (\nu - \nu_0)/b = 1, 2, 3, \ldots, 15$.

An IBM 1620 electronic computer was used.\(^1\)

A $\Delta T = 1\%$ has been assumed. For other values of $\Delta T$, $\Delta A/A$ can easily be calculated, as $\Delta A/A$ is proportional to $\Delta T$.

From this table it can be seen that

a. for small $(\nu - \nu_0)/b$ values the minimum $\Delta A/A$ is equal to $2.8 \Delta T$, which is reached for $E_0 = 0.5$, but this is not very realistic, as for small $(\nu - \nu_0)/b$ values only the smaller part of the absorption band is integrated. For increasing integration range, the optimum $E_0$ value increases from $E_0 = 0.43$ (for $(\nu - \nu_0)/b = 0$) to $E_0 = 1.2$ (for $(\nu - \nu_0)/b = 15$);

b. for reasonable integration limits (for instance $(\nu - \nu_0)/b = 7$ which is equivalent to an integration of about $90\%$ of the band area), a smallest $\Delta A/A = 4.4 \Delta T$ can be achieved for $E_0 = 1.0$;

\(^1\) The use of the facilities of the Dpt of Mathematics is gratefully acknowledged.
c. if it is possible to integrate the "whole" band - 99% of the band will be measured with (v-v₀)/b = 15 - the inaccuracy will increase to at least 6.3 ΔT for an optimum E₀ = 1.2.

Stray light has been neglected so far, but must be considered as well. If we put the apparent transmission T' equal to T' = I/I₀, the real transmission T can be written as T = (1 - p)/I₀ - p.

Here p stands for the intensity of the stray light. (It is assumed that p is constant over the frequency range of the absorption band, and that p is independent of the sample).

In order to find the explicit relation between T and T' we write:

\[
\begin{align*}
T &= \frac{I - p}{I_0 - p} = \frac{I}{I_0} - \frac{p}{I_0} = \frac{I + pI/I_0}{I_0} - \frac{p}{I_0} \\
&= \frac{I}{I_0} + \frac{p}{I_0} \frac{I/I_0}{I_0} - \frac{p}{I_0} = T' - \frac{p}{I_0}(1 - T)
\end{align*}
\]

If p/I₀ is put equal to q (100.q = percentage stray light) we find

\[
T = T' - q(1 - T)
\]
resulting in an extinction error

\[
\Delta E = E' - E = -\log T'/T = -\log \{1 + q(10^E - 1)\}
\]

which leads to an intensity error

\[
\Delta A = \frac{\int_{-a}^{+a} \Delta E d\nu}{A} = -0.434 \int_{-a}^{+a} \frac{\ln \{1 + q(10^E - 1)\} d\nu}{\int_{-a}^{+a} E d\nu}
\]

This function has been calculated for a number of E₀, q and a values. Table VII-2 shows the results for q = 0.01 (1% stray light), E₀ = 0.1, 0.2... ...1.8, and a = (ν-ν₀)/b = 0, 1, 2, ......... 7, 8, 10, 12 and 14.

The following general conclusions may be drawn:

1. the stray light error increases continuously with increasing E₀ (at constant integration limits);

1) The use of the facilities of the Dpt of Mathematics is gratefully acknowledged.
### Table VII-1

**Influence of a Photometric Accuracy of $\Delta T = 1\%$ on Relative Errors in Integrated Intensities ($\Delta A / A$ in %).**

<table>
<thead>
<tr>
<th>$\delta$</th>
<th>0.1</th>
<th>0.2</th>
<th>0.3</th>
<th>0.4</th>
<th>0.5</th>
<th>0.6</th>
<th>0.7</th>
<th>0.8</th>
<th>0.9</th>
<th>1.0</th>
<th>1.1</th>
<th>1.2</th>
<th>1.3</th>
<th>1.4</th>
<th>1.5</th>
<th>1.6</th>
<th>1.7</th>
<th>1.8</th>
<th>1.9</th>
<th>2.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.6</td>
<td>0.4</td>
<td>0.2</td>
<td>0.2</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>3.1</td>
<td>3.1</td>
<td>3.1</td>
<td>3.1</td>
<td>3.1</td>
<td>3.1</td>
<td>3.1</td>
<td>3.1</td>
<td>3.1</td>
<td>3.1</td>
<td>3.1</td>
<td>3.1</td>
<td>3.1</td>
</tr>
<tr>
<td>2</td>
<td>0.9</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>3</td>
<td>1.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
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<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>4</td>
<td>1.9</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
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<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>5</td>
<td>2.4</td>
<td>1.4</td>
<td>1.4</td>
<td>1.4</td>
<td>1.4</td>
<td>1.4</td>
<td>1.4</td>
<td>1.4</td>
<td>1.4</td>
<td>1.4</td>
<td>1.4</td>
<td>1.4</td>
<td>1.4</td>
<td>1.4</td>
<td>1.4</td>
<td>1.4</td>
<td>1.4</td>
<td>1.4</td>
<td>1.4</td>
<td>1.4</td>
</tr>
</tbody>
</table>

2. the stray light error decreases with increasing integration range (at constant $E_0$);

3. with increasing $E_0$ the stray light error increases slower for larger integration ranges;

4. the stray light error according to VII-13 is in any case larger than $q$:

   For reasonable conditions like $q = 0.01$, $E_0 = 1.0$ and $a = 7$, $\Delta A / A$ amounts 0.022.

Function VII-13 has also been calculated for variable $q$; $q$ values of 0.001, 0.003, 0.01 and 0.03 were chosen. These results are not given because...
(except for a combination of low $a$-values and high $E_0$-values, which combination is of little interest) it was found that:

5. Stray light error according to VII-13 is proportional to $q$.

**VII-2. The absolute intensities of hydrocarbon-type $\text{CH}_2$ and $\text{CH}_3$ deformations**

For 19 aliphatic hydrocarbons (Phillips Hydrocarbons, research grade), absolute intensities were measured between $1330-1410$ cm$^{-1}$ (symmetrical $\delta$CH$_3$) and between $1410-1510$ cm$^{-1}$ (asymmetrical $\delta$CH$_3$ plus $\delta$CH$_2$); see Table VII-3.

<table>
<thead>
<tr>
<th>NAME OF COMPOUND</th>
<th>Number of $\text{CH}_2$ groups</th>
<th>Number of $\text{CH}_3$ groups</th>
<th>$10^8 A$ (cm$^2$/moleculesec) $\lambda=1230$ cm$^{-1}$</th>
<th>$10^8 A$ (cm$^2$/moleculesec) $\lambda=1310-1510$ cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexane</td>
<td>6</td>
<td>-</td>
<td>16.9</td>
<td>-</td>
</tr>
<tr>
<td>n-hexane</td>
<td>6</td>
<td>2</td>
<td>17.0</td>
<td>3.8</td>
</tr>
<tr>
<td>n-heptane</td>
<td>5</td>
<td>2</td>
<td>19.8</td>
<td>6.8</td>
</tr>
<tr>
<td>n-octane</td>
<td>7</td>
<td>2</td>
<td>23.8</td>
<td>7.4</td>
</tr>
<tr>
<td>n-decanes</td>
<td>9</td>
<td>2</td>
<td>26.6</td>
<td>7.4</td>
</tr>
<tr>
<td>2,2-di-Me-butane</td>
<td>1</td>
<td>4</td>
<td>21.2</td>
<td>14.9</td>
</tr>
<tr>
<td>Cycloheptane</td>
<td>4</td>
<td>-</td>
<td>9.5</td>
<td>-</td>
</tr>
<tr>
<td>Hexene-1</td>
<td>3</td>
<td>1</td>
<td>14.9</td>
<td>3.07</td>
</tr>
<tr>
<td>Me-cyclcopentane</td>
<td>4</td>
<td>1</td>
<td>12.3</td>
<td>3.09</td>
</tr>
<tr>
<td>Octene-1</td>
<td>5</td>
<td>1</td>
<td>17.9</td>
<td>4.02</td>
</tr>
<tr>
<td>Me-cyclohexene</td>
<td>5</td>
<td>1</td>
<td>18.8</td>
<td>3.17</td>
</tr>
<tr>
<td>2,2-di-Me-butane</td>
<td>-</td>
<td>4</td>
<td>20.6</td>
<td>15.1</td>
</tr>
<tr>
<td>Trans-4-Me-pentene-2</td>
<td>-</td>
<td>3</td>
<td>10.4</td>
<td>8.61</td>
</tr>
<tr>
<td>2-Me-pentene-1</td>
<td>2</td>
<td>2</td>
<td>20.7</td>
<td>6.98</td>
</tr>
<tr>
<td>5-Me-hexane</td>
<td>3</td>
<td>3</td>
<td>20.3</td>
<td>9.79</td>
</tr>
<tr>
<td>2-Me-pentane</td>
<td>2</td>
<td>3</td>
<td>16.7</td>
<td>10.8</td>
</tr>
<tr>
<td>2,4-di-Me-pentane</td>
<td>1</td>
<td>4</td>
<td>22.4</td>
<td>15.2</td>
</tr>
<tr>
<td>2,3,4-tri-Me-pentane</td>
<td>1</td>
<td>5</td>
<td>21.5</td>
<td>19.6</td>
</tr>
<tr>
<td>2,2,5-tri-Me-hexane</td>
<td>2</td>
<td>5</td>
<td>29.5</td>
<td>20.5</td>
</tr>
</tbody>
</table>

The group-intensities for the three vibrations, which fit in best with the figures of this Table are those given in Table IV-6.

It may be noted that the integration limits chosen roughly correspond with a $(\nu-\nu_0)/b = 7$ value. One might be inclined therefore, to add 10% to the intensities measured as a wing correction (see also preceding section). We have not made this correction, seen the fact that neighbouring absorption bands, which we do not wish to measure, will nevertheless have an intensity contribution in the region measured. It can only be hoped that this contribution compensates for the 10% wing absorption lost.

For a number of single, non-overlapping bands in the $1380$ cm$^{-1}$ region, the
absolute intensity was also calculated from \( A = \pi \epsilon_0 b \), and surprisingly enough, these intensities corresponded well with those measured by integration the 1330-1410 cm\(^{-1}\) region. This supports and justifies the integration limits chosen.

VII-3. The infrared instrument

As mentioned before, a Hilger and Watts H 800 spectrophotometer was used for all the infrared measurements. Unless stated otherwise, the instrument was equipped with a NaCl prism, combined with a so-called R\(_4\) wavenumber drive cam. This cam produces the spectra on a scale linear in cm\(^{-1}\). Below 2000 cm\(^{-1}\), the wavenumber scale is 4x expanded. The scan speed normally used was 60 minutes for the 4000-650 cm\(^{-1}\) range, which correspond with about 2.2 cm\(^{-1}\)/sec for the 4000-2000 cm\(^{-1}\) range and 0.50 cm\(^{-1}\)/sec for the 2000-650 cm\(^{-1}\) range. The instrument has a slit programmer, which was adjusted to a constant-energy programme. An initial slitwidth of 0.06 mm at 4000 cm\(^{-1}\) was used. The theoretical resolutions, as calculated from Van Zandt William's* equation are given in Table VII-4.

<table>
<thead>
<tr>
<th>( \nu ) (cm(^{-1}))</th>
<th>Slitwidth (mm)</th>
<th>Optical slit ((\Delta \nu)_{\text{opt}}) in cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>4000</td>
<td>0.060</td>
<td>31</td>
</tr>
<tr>
<td>3600</td>
<td>0.068</td>
<td>31</td>
</tr>
<tr>
<td>3200</td>
<td>0.073</td>
<td>27</td>
</tr>
<tr>
<td>2800</td>
<td>0.096</td>
<td>24</td>
</tr>
<tr>
<td>2400</td>
<td>0.107</td>
<td>20</td>
</tr>
<tr>
<td>2000</td>
<td>0.123</td>
<td>11</td>
</tr>
<tr>
<td>1800</td>
<td>0.200</td>
<td>6</td>
</tr>
<tr>
<td>1600</td>
<td>0.208</td>
<td>4</td>
</tr>
<tr>
<td>1400</td>
<td>0.216</td>
<td>2.5</td>
</tr>
<tr>
<td>1200</td>
<td>0.224</td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>0.232</td>
<td></td>
</tr>
<tr>
<td>900</td>
<td>0.240</td>
<td></td>
</tr>
</tbody>
</table>

For some special purposes like the \( \equiv \text{C-H} \) stretching frequency, discussed in Chapters IV and V, the NaCl prism offered too low a resolution in the region of interest (25 cm\(^{-1}\) at 3000 cm\(^{-1}\)). Therefore a grating of 7,500 l.p.i. was installed as well as the appropriate cam. This greatly improved the resolution. Using a slitwidth of 0.3 mm, a resolution of \((\Delta \nu)_{\text{opt}} = 1.5\) cm\(^{-1}\) was calculated.

Using this grating, the isotope fine structure of the HCl stretching vibration which amounts to 1.9 cm\(^{-1}\), could be very well resolved. Spectra to be integrated were separately run on a tenfold expanded wave-
number scale (32 cm chartlength corresponding with 100 cm⁻¹).
Concentration and cell thickness were chosen in such a way that the maximum extinction was about 0.8 (see preceding sections).
In the reference beam, a variable cell was always used. Its thickness was adjusted to the cell thickness of the sample cell minus the partial thickness of the solute.

VII-4. The Ultraviolet spectrophotometer

The Cary 14 spectrophotometer, which was used for the U.V. measurements, is a well-known high-performance instrument, so little need be said about it.
Slit control and photomultiplier voltage were chosen to give a resolving power of 2 Å at 190 nm, combined with an electronic noise of $\Delta E/E = \pm 0.01$. This compromise was preferred to the alternative 10 Å resolution, combined with a noise $\Delta E/E = \pm 0.002$; by keeping the slitwidth as small as possible, the influence of any stray light was reduced. Stray light was shown to be absent above 190 nm, at 186 nm the effect of the stray light amounted to about 4%, for which effect a correction could be made.
The photometrical reproducibility at 190 nm was about 1% (in extinction units).
As the preparation of samples gave rise to great difficulties, the absolute accuracy of the extinction coefficients is somewhat lower (± 5%).

VII-5. The NMR spectrometer

A commercial 40 Mc NMR spectrometer, made by Perkin Elmer Ltd, was used for all our NMR measurements. The instrument has a permanent magnet of approximately 9,400 gauss. Because of the large temperature dependence of the magnetic field, the magnet is placed in an air thermostat.
Field fluctuations caused by temperature changes are never more than ± 0.05 milligauss (± 0.2 cps). Field drift is less than 0.25 milligauss (1 cps) per hour. After the installation of the instrument, strong magnetic field fluctuations were observed. It could be proved that these fluctuations had an external origin, namely the current fluctuations from the nearby railway yard. The fluctuations inside the building were about ten times stronger than outside the building (as measured with a magnetic fluxmeter). It was therefore concluded that we were not dealing with the direct magnetic field generated by the overheadlines-train-rail loop, but rather with currents flowing back through the soil, which enter the laboratory through the steel of the reinforced concrete of the building-skeleton.
In order to compensate these external field fluctuations, Perkin Elmer
developed a flux-gate stabilizer. This instrument consists of three major parts: a sensing element, the electronical unit and a compensating coil.

The sensing element, which is sensitive to magnetic field changes and their direction is mounted sideways the magnet-thermostat box, about halfway between magnet and floor. The sensing element must be placed precisely at a spot where the total magnetic field is zero, which spot can be found with the aid of the flux-gate itself. The electronical unit comprises the supply for the sensing element, an amplifier and a feed-back loop, The latter sends a D.C. signal into a coil, which is suspended in the magnet gap. This current creates in the magnet gap an extra magnetic field, which neutralizes the external field fluctuation. The compensator was shown to have an efficiency of 95% for fluctuations, whose origin is in the direction of the magnet axis, and at least 5 yards removed from the magnet. For shorter distances or fluctuation sources off the magnet axis, the efficiency may be less. Incomplete compensation or even overcompensation may then occur. For instance, the effect of a steel gascylinder passing by at distance of two or three yards, will still influence the magnetic field prevailing in the gap.

As to the disturbance caused by the D.C. operated railways, the flux-gate stabilizer proved to be most succesful in restoring the field stability.

Only for very precise work — such as the fine structure of the olefinic proton absorption, discussed in Chapter V — where a field stability of ± 0.1 cps (± 0.02 milligauss) is required, the external field fluctuations were still a nuisance, although after compensation, they were never more than 0.5 cps peak to peak. Most of the final spectra, reproduced in the Chapters IV and V, have therefore been obtained on Monday mornings between 01.00 and 5.30 a.m., the only hours in week when the railway current is switched off. The homogeneity of the magnetic field was always better than 1:10^8. This could be derived either from the linewidth of the acetaldehyde quartet or from the relaxation-wiggle pattern of the acetaldehyd doublet. The best homogeneity ever obtained with our instrument was 4.5:10^9 (0.18 cps linewidth). The homogeneity instability in time was less than a factor of 2 in 24 hours.

Nine adjustable Golay coils, placed in the magnet gap, provided the necessary means for field homogenizing.

With another set of coils the magnetic field can be increased or decreased to an extent exactly known. This variability may be ± 11 Kc (± 3.75 gauss), but only the "decade field shift" control (with steps of 100.0 cps) and the field shift fine control (0.0 to 100.0 cps) was used.
The field sweep, and therefore the spectrum, can be recorded either on a cathode-ray oscilloscope or on a pen-recorder, which have the timeconstant control, scale factor and Y-axis zero setting in common. The essential potentiometer for the recorder field sweep is mechanically coupled to the recorder drum, so that scan speed can be changed during a run, without the risk that chart speed and scan speed will get out of phase. A 400cps audio-oscillator is built in, with which the field shift and field sweep calibrations can be checked.

The sample tubes consist of this walled glass tubes of about 15 cm length and 4.6 mm outside diameter. In order to attain the high resolution of $1 \times 10^8$ or better, the sample has to be spun. A thermostated air jet drives a polythene spinner, which is fixed on to the top of the sample tube. Two teflon side Bearings and one bottom-bearing keep the sample tube in position; 300 µl liquid is the optimum sample quantity required.

A simple electronic integrator, whose signal is fed into the pen-recorder system, enables the integration of the absorption bands with a reproducibility of about $\pm 5\%$. This accuracy is sufficient – at least for small and medium-size molecules – to count the relative number of protons of the functional groups present in the molecule.
SUMMARY

The purpose of the investigations, described in this thesis was to contribute to the knowledge of the monoterpenes by means of a combination of Physical Methods. These methods comprise kinetical experiments, gas-liquid chromatography, distillation, infrared-, ultra violet and nuclear magnetic resonance spectroscopy.

In Chapter I the design of a micro reactor for reactions in the gas-phase is described. The very particular dimensioning and construction guarantee that residence time, reaction temperature and reaction rate can be measured precisely and with the greatest accuracy.

Chapter II contains a discussion about acetate pyrolysis. New arguments and evidence in favour of the mono-radical reaction mechanism are put forward. It is shown that the three isomeric acetates: linalyl acetate, neryl acetate and geranyl acetates, each having a $\beta,\gamma$ C=C bond, have one and the same activated state. This could be explained by the hypothesis that the three primary monoradicals are intermediates to a common anti-bonding state. The activation energies of two acetates were measured, while the pyrolysis products of eight acetates were studied.

Chapter III describes the distillation equipment, the preparative-scale gas-chromatograph, and a macro pyrolysis reactor; moreover, the analytical gaschromatograph and the working methods followed. 18 Monoterpenes (alcohols, esters, and hydrocarbons) were obtained by distillation in a high degree of purity. Furthermore the refractive indices, densities, optical rotation and retention indices of these 18 terpenes were measured.

Chapter IV handles about a study of the above mentioned 18 terpenes by means of infrared-, ultraviolet- and nuclear magnetic resonance spectroscopy. Known correlations were tried out and improved if possible. A number of new correlations is suggested. Special attention was paid to the analysis of the absorption intensities.
Cis-trans isomerism of trisubstituted ethylene derivatives forms an important feature of terpene chemistry, to which up to now – due to a lack of suitable separation and identification methods – little attention has been paid. For this reason, Chapter V refers to an infrared and nuclear magnetic resonance study of three pairs of cis-trans isomers of the trisubstituted ethylenic type. For this purpose model compounds from the API collection were used.

For the assignment of the cis-trans configuration ten rules were developed. Nine of these are differential rules; both isomers are necessary to determine which is which. The tenth correlation, based on a long-range spin-spin coupling effect, makes it in principle possible to assign either the cis- or the trans configuration, even if only one of the two isomers is known.

It proved that the API cis-trans labelling of the 3-methyl-3-hexenes should be the other way around.

In Chapter VI some structural aspects of "known" terpenes are discussed, as well as the structures of a few new products. Concerning the neryl and geranyl structures it was still impossible to determine which has the cis- and which the trans configuration. However, the main arguments are in favour of the cis configuration for neryl.

It is shown that of the two allo ocimenes known, the low-boiling isomer (allo ocimene I) has the 4-trans-6(7)-cis structure, and the high-boiling isomer (allo ocimene II) has the 4-trans-6(7)-trans structure.

By pyrolysis of tetrahydrogeranyl acetate a new terpene hydrocarbon was obtained having the 3,7-dimethyl-octene-1 structure.

It was found that the main compound, isolated from the pyrolysis products of citronellyl acetate does not have the 3,7-dimethyl-octadiene structure expected, but the \( \Lambda^\delta \)-p-menthene structure.

The experimental and instrumental details of the spectrometrical measurements are compiled in Chapter VII.

Calculations were made as to the influence of photometrical accuracy and of stray light on the accuracy of intensities of infrared bands integrated.
SAMENVATTING

De in dit proefschrift beschreven onderzoekingen hadden tot doel, om met een combinatie van fysische methoden een bijdrage te leveren tot de kennis omtrent de monoterpenen. Deze methoden omvatten reactiekinetische experimenten, gas-vloeistof-chromatografie, destillatie, infrarood-, ultra-violett- en kernspinresonantie-spectrometrie.

In hoofdstuk I wordt besproken het ontwerp van een microreactor voor reacties in de gasfase, welke reactor door zijn bijzondere dimensionering en constructie een nauwkeurig gedefinieerde verblijftijd en reactietemperatuur waarborgt.

Hoofdstuk II is gewijd aan een discussie over de acetaatpyrolyse. Nieuwe argumenten en bewijsmateriaal worden aangevoerd ten gunste van een monoradicaal reactiemechanisme. Er wordt aangetoond dat de drie isomere acetaten: linalylacetaat, nerylacetaat en geranylacetaat – die alle drie een β,γ C=C binding ten opzichte van de acetaatgroep bezitten – dezelfde geactiveerde toestand hebben. Dit wordt verklaard met de hypothese dat de drie primaire monoradicalen slechts intermediairen zijn naar een gemeenschappelijke antibonding-toe­stand. Van twee acetaten werden de activeringsgrootheden gemeten, terwijl van zeven acetaten de pyrolyse-produkten werden bestudeerd.

In hoofdstuk III worden distillatie-apparatuur, een preparatieve gaschromatograaf en een macro-pyrolysereactor beschreven, en tevens de gebruikte analytische gaschromatograaf en de daarbij toegespaste werkwijzen. Door distillatie werden 18 monoterpenen (alcoholen, acetaten en koolwaterstoffen) verkregen in een hoge mate van zuiverheid. Van deze 18 stoffen werden de brekingsindices, dichtheden, optische rotaties en retentie­indices gemeten.

Cis-trans-isomerie van trigesubstitueerde ethyleenderivaten vormt een belangrijk aspect van de terpeenchemie, waaraan tot dusverre – bij gebrek aan geschikte scheidings- en identificatiemethoden – weinig aandacht is geschonken.

Hoofdstuk V is daarom gewijd aan een infrarood- en kernspinspectrometrische studie van 3 paren cis-trans-isomeren van het trigesubstitueerde ethyleenotype. Modelstoffen van de API-collectie werden hiervoor gebruikt. Tien correlaties werden ontwikkeld voor het toekennen der cis- c.q. transstructuur. Negen dezer correlaties zijn verschilregels; beide isomeren zijn daarbij nodig, teneinde te kunnen uitmaken welke welke is. De tiende correlatie, berustend op een long-range spin-spin koppelingseffect, is in principe in staat de cis- of transstructuur toe te kennen ook wanneer slechts één der twee isomeren bekend is.

Van de door het API toegekende cis- en transpredicaten van de 3-methyl-3-hexenen werd aangetoond dat deze naamgeving dient te worden omgekeerd.

In hoofdstuk VI worden structuurfacetten besproken van enige terpenen, waarvan de structuur niet of niet volledig bekend was. Omtrent de cis-trans-isomerie van de neryl- en geranylstructuren blijkt nog steeds geen definitieve uitspraak mogelijk te zijn. De zwaarste wegende argumenten geven echter de cis-configuratie voor neryl aan. Van de twee bekende allo-ocimenen werd aangetoond dat de laagkokende isomeer (allo-ocimeen-I) de 4-trans, 6(7)-cis structuur heeft, terwijl de hoger kokende isomeer (allo-ocimeen-II) de 4-trans, 6(7)-trans structuur bezit.

Door pyrolyse van tetrabydrogeranylacetaat werd een nieuwe koolwaterstof verkregen, die de 3,7-dimethyl-octeen-1 structuur heeft. Van het geïsoleerde hoofdproduct van de pyrolyse van citronellylacetaat werd aangetoond dat deze component niet de verwachte structuur heeft van 3,7-dimethyl-1,6-octadien, maar die van Δ²⁺(8)-p-mentheen.

In hoofdstuk VII zijn de experimentele en instrumentele bijzonderheden over de spectrometrische metingen verzameld. Enkele berekeningen zijn gemaakt omtrent de invloed van fotometrische nauwkeurigheid en van strooilicht op de geïntegreerde intensiteiten van infrarood-absorptiebanden.
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GLOSSARY OF SYMBOLS

A Absolute intensity of infrared (or ultraviolet) absorption band; equal to \( \int_{-\infty}^{\infty} \epsilon \, d\omega \), \( (\text{cm}^2 / \text{molecule sec}) \).

a Dimensionless frequency range; equal to \( (\nu - \nu_0)/b \).

\([\alpha]_{589}^{21.5}\) Molecular optical rotation at 589 nm and 21.5°C (degrees rotation).

b Half bandwidth at half the extinction height (cm\(^{-1}\)).

b.p. 20 Boiling point at 20 mm pressure (°C).

C Concentration at reactor entrance.

C\(_t\) Concentration in the reactor after residence time t.

c Concentration (Mole/l).

cm\(^{-1}\) Number of waves per cm.

cps Cycles per second.

D Diffusion constant (cm\(^2\)/sec).

D\(^*\) Virtual diffusion constant (cm\(^2\)/sec).

d Tube diameter (cm).

\(d_{25}\) Density at 25°C with reference to unity density for water of 4.00°C (g/ml).

\(\Delta\) Indicates error

\(\Delta\) Indicates C=C double bond in chemical formulae.

\(\delta\) Deformation mode of vibration.
\( \delta \) NMR chemical shift; equal to \( \Delta H/H \times 10^6 \), relative to some reference substance (ppm).

\( E \) Extinction, defined by \( E = -10 \log T \).

\( E' \) Apparent extinction; straylight being neglected.

\( E^* \) Activation energy (kcal/Mole).

\( E_0 \) Extinction at wavelength of maximum absorption.

\( e \) Base of natural logarithm; \( e = 2.7183 \).

\( \epsilon \) Molecular extinction coefficient (cm\(^2\)/Mole.1000).

\( \epsilon' \) Apparent extinction coefficient; not corrected for finite optical slit width.

\( \epsilon_{\text{max}} \) Extinction coefficient at wavelength of maximum absorption.

\( \epsilon^* \) Equal to \( (-\ln T)/c \).

\( 1 - f \) Conversion rate; equal to \( 1 - C_f/C_o \).

\( h \) Planck's constant; \( h = 6.625 \times 10^{-27} \) ergsec.

\( I \) Intensity of light beam after passage through an absorbing sample.

\( I_0 \) Intensity of light beam before the passage through a sample.

IR Infrared

\( I_x \) Retention index; for definition see section III-4.

\( J \) Spin-spin coupling constant (cps).

\( k \) Reaction rate (sec\(^{-1}\)).

\( k' \) Apparent reaction rate (see equation I-10).

\( k^* \) Bolzmann's constant; \( k^* = 1.3805 \times 10^{-16} \) erg \(^*\)K\(^{-1}\).
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>Total length of reactor (cm).</td>
</tr>
<tr>
<td>l</td>
<td>Cell thickness (cm).</td>
</tr>
<tr>
<td>$\lambda_{max}$</td>
<td>Wavelength of maximum absorption; used in UV only (nm).</td>
</tr>
<tr>
<td>Mc</td>
<td>Megacycles ($10^6$ cps).</td>
</tr>
<tr>
<td>m</td>
<td>Infrared band of medium intensity; $\varepsilon'$ between 10 and 40.</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Average value of any physical constant or measurement.</td>
</tr>
<tr>
<td>$n_{D}^{25}$</td>
<td>Refractive index in air at 589 nm at 25.0°C.</td>
</tr>
<tr>
<td>nm</td>
<td>Nanometer ($10^{-9}$ m).</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance.</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Frequency (cm(^{-1})).</td>
</tr>
<tr>
<td>$\nu_{0}$</td>
<td>Frequency of maximum absorption.</td>
</tr>
<tr>
<td>$(\Delta\nu)_{1/2}$</td>
<td>Bandwidth at half the extinction height; equal to $2b$ (cm(^{-1})).</td>
</tr>
<tr>
<td>o.o.p.</td>
<td>Out-of-plane (deformation).</td>
</tr>
<tr>
<td>p</td>
<td>Intensity of stray light.</td>
</tr>
<tr>
<td>q</td>
<td>Stray light factor; equal to $p/I_{o}$.</td>
</tr>
<tr>
<td>R</td>
<td>General gas constant; equal to $k^p N$; $R = 8.3170 \times 10$ erg/°K Mole.</td>
</tr>
<tr>
<td>$\Delta S^o$</td>
<td>Activation entropy (cal degree(^{-1}) Mole(^{-1})).</td>
</tr>
<tr>
<td>s</td>
<td>Infrared band of strong intensity ($\varepsilon'$ between 40 and 200).</td>
</tr>
<tr>
<td>sh</td>
<td>Shoulder (on infrared band).</td>
</tr>
<tr>
<td>T</td>
<td>Transmission $T = I/I_{o}$.</td>
</tr>
<tr>
<td>T</td>
<td>Absolute temperature (°K).</td>
</tr>
</tbody>
</table>
T'  Apparent transmission; stray light being neglected.

\( t \)  Time (sec).

\( t \) or \( r \)  Average total residence time (sec).

\( r \)  NMR chemical shift measure; \( r = 10 - \delta \), tetramethylsilane being taken as the reference substance.

\( \Delta r_{tc} \)  Difference between the \( r \) value of a certain signal in the NMR spectrum of a "trans" compound and the \( r \) value of the corresponding signal in the spectrum of analogous "cis" compound.

UV  Ultraviolet.

\( u \)  Linear gas velocity (cm/sec).

vs  Infrared band of very strong intensity (\( \epsilon' \) larger than 200).

vw  Infrared band of very weak intensity (\( \epsilon' \) below 2).

w  Infrared band of weak intensity (\( \epsilon' \) between 2 and 10).

\( \bar{x} \)  Average travelling path.

*  See list of literature references.

1)  See footnote.
Levensbeschrijving


In september 1956 behaalde hij het kandidaatsdiploma (letter f) en na voortgezette studie onder leiding van de hoogleraren Böttcher, Oosterhoff en Havinga in oktober 1958 het doctoraal examen.

Na een stage bij Dr. Bell (F.R.S.) van het "Physical Chemistry Laboratory" te Oxford, Engeland, werd hij maart 1959 benoemd tot wetenschappelijk ambtenaar aan de Technische Hogeschool te Eindhoven. Sedertdien is hij als medewerker van professor Keulemans werkzaam aan diens Laboratorium voor Instrumentele Analyse, alwaar hij speciaal belast werd met de inrichting en leiding van de molecuul-spectrometrische groep. In 1961 kon een aanvang gemaakt worden met een systematisch onderzoek op het gebied der monoterpenen, welk onderzoek tot dit proefschrift heeft geleid.

Zowel de breedte van dit onderzoek alsmede de omstandigheid dat het verricht werd in een laboratorium-in-opbouw maakten de hulp van velen, meer dan anders, onontbeerlijk. Met grote dankbaarheid zij daarom de loyale medewerking vermeld die de schrijver van velen mocht ondervinden. Hen allen te noemen is niet wel mogelijk; een uitzondering wil hij echter maken voor zijn hoofd-assistente mej. L. Ehrnreich en voor de heren Ir. R. Deelder en Ir. J. de Haan, wegens de aanzienlijke bijdragen die zij leverden bij het verzamelen der experimentele resultaten.
STELLINGEN

1. Alhoewel een infraroodspectrum per definitie twee-dimensionaal is, bestaat er naast een zeer uitgebreide literatuur over frequentieanalyse nauwelijks belangstelling voor de analyse van de intensiteitsdimensie. Zowel de huidige ontwikkelingen in de infraroodinstrumentatie als de moderne snelle rekenmethoden maken het thans mogelijk om door middel van intensiteitsanalyse een nieuwe impuls te geven aan de infraroodspectrometrie.

2. De methode van Böttcher om uit meting van brekingsindices en dichtheden elektronenpolarizerbaarheden van ionen te berekenen, is onderhevig aan enige twijfel voor wat betreft de absolute betrouwbaarheid der resultaten. Door een éénmalige serie metingen aan een set iso-elektronische structuren is het echter in principe mogelijk deze systematische fout(en) te elimineren en de methode "selfconsistent" te maken.


3. Bouma maakt onder bepaalde omstandigheden gebruik van het begrip "dominerende golflengte" op een wijze, welke niet in overeenstemming is met de door hemzelf gegeven definities betreffende "contourlijn der spectrale kleuren", "witpunt" en "dominerende golflengte".

P.J. Bouma, "Kleur en kleurindrukken", Meulenhoff & Co, Amsterdam 1946, paragrafen 20, 22, 23 en 41

4. Kernspinresonantie is, tot dusver, de enige methode die op snelle wijze direct bewijs kan geven omtrent de cis- of transconfiguratie van een trigesubstitueerd ethyleen.

Dit proefschrift, Hoofdstuk V
5. De infrarood-spectrometrische methode, door Gössl gebruikt om de mate van "kristalliniteit" van ethyleen-propyleen co-polymeren aan te geven, is principieel onjuist en geeft aanleiding tot misleidende conclusies.

   Th. Gössl, Die Makromolekulare Chemie 42 (1960), 1

6. Het experiment, beschreven door Scheer, om aan te tonen dat bij de pyrolyse van acetaten in een glazen reactor wandeffecten kunnen optreden, is niet toereikend om een dergelijke conclusie te rechtvaardigen.

   J. C. Scheer, "De Pyrolyse van Alkylacetaten in de Gasfase", proefschrift Amsterdam 1961, blz. 51

7. Aan de empirisch gevonden lineaire betrekking tussen de logaritmen van gaschromatografische retentietijden en de reciproque kookpuntstemperaturen van een reeks analoge stoffen mag geen fysische betekenis worden toegekend, gezien het lineaire verband tussen T en 1/T in het desbetreffende temperatuurtraject (400-500 °K).


   M. H. Klouwen, R. ter Heide, J. Chromatography, 7 (1962), 297

8. Het verdient aanbeveling, dat gehuwde vrouwen met een academische opleiding gestimuleerd worden een deel van hun tijd te besteden in een bij hun vorming passende functie.

   Mededelingen van de Nederlandse Vereniging van Vrouwen met Academische Opleiding 27, (1961), no 4 en 28 (1962), no 4

9. Een actie, zoals opgezet door de stichting 0-11, om normale weggebruikers in te schakelen bij de verkeerscontrole, is beslist ongewenst.


10. De Nederlandse universiteiten dienen hun opleidingen in de fysico-chemische richting drastisch te herzien, speciaal in verband met het heden ten dage zeer intensieve gebruik van fysische meetmethoden in de chemie.