SECTION B.

ISOMERISATION OF 3-CARENE.

This section is devoted to:

Part I : Literature survey
Part II : Experimental- Isomerisation of 3-carene
Part III : Discussion and Reaction mechanism and
Part IV : Summary.

PART I-LITERATURE SURVEY:

It was not until 1945 that Rudakov and Artamonov\(^1\) made a comprehensive study of the isomerisation of 3-carene using activated clay catalyst. The reaction mixture contained the isomers dipentene, terpinolene, \(\alpha\)-terpinene and traces of meta-compounds and also p-cymene, p-3-menthene, polymeric products besides un-reacted 3-carene.

In 1949 Bhushan and Sharma\(^2\) effected the isomerisation of a mixture of 3-carene and \(\Delta\)-carene\(^*\) obtained from Indian turpentine oil by heating it for 1½ hours in a steel autoclave under a pressure of 75 lbs. per sq.inch. The steam volatile portion of the

* \(\Delta\)-carene is a doubtful constituent of Indian turpentine oil (Cf.p.8) and in this discussion only the transformations of 3-carene are considered.
reaction mixture amounted to 91.2%, with $\alpha^{20}_D 1.4783$, $d^{20} 0.8538$, $(a)_D - 3.3^\circ$, iodine $N_0 296$ and 82% boiled between 170-177°. It was a colourless oil with lemon odour and its boiling range and other constants suggested the presence of $\alpha$-terpinene (probably of $\gamma$-terpinene also) which was confirmed by Raman lines.

Very recently a comprehensive investigation of the action of sulphuric acid on pure 3-carene has been made by Hellstrem and Ottar. Pure 3-carene (obtained from sulphate turpentine) was heated to boiling with a small amount of sulphuric acid. There was darkening of the mixture. A mono-terpene, boiling at 170-200° and a diterpene, $b_{25} 193.5^\circ$, $n^{20} 1.5180$, $d_{20} 0.9498$, $(a)^{20}_D 0.0^\circ$ (abs. alc.), molecular weight, 280 (in camphor), were isolated. The proportion of the isomerisation product to the dimerisation product was related to the concentration of sulphuric acid, the diterpene fraction increasing linearly with acid concentration (1 to 9%).

The isomerisation of 3-carene (I) gave primarily the following hydrocarbons:

![Diagram of hydrocarbons](image)

Ozonolysis yielded acetone, confirming the existence of a
\(-\text{C.N}_2\) group. Derivatives confirmed (A) as dipentene, (B) as
\(\alpha\)-terpinene, (C) as sylvestrene and (D) as isocarvestrene (?)..

Apart from the abortive attempt to isomerise 3-carene
to allo-ocimene by passing the vapours of the terpene over frag­
ments of suprex glass and reduced copper at 345-350° and 360-400°
respectively\(^1\), probably the only isomerisation of 3-carene in the
vapour phase is that reported by Bhushan and Sharma\(^2\). Using a
copper pyrolytic tube packed with activated thorla catalyst at
450° and liquid hourly space velocity of 0.14, 3-carene yielded
a lemon-smelling oil (97.2%). The pyrolysate had \(n^\text{D}_{20} 1.4768,\)
d\(\text{D}_{20} 0.9429, (a)_{D} + 5.4°, \text{iddlo.} \text{No.317.70 and 73% boiled at}
178-183°. Isolation of the fraction of the pyrolysate boiling at
179-181° by careful fractionation and subjecting it to Raman
spectra, gave displacements 1650 and 1682 cm\(^{-1}\) from which it was
adduced that dipentene was the chief product and that \(\alpha\)-terpinene
and 3-carene were absent. Preparation of tetrabromide, m.p.124°,
and of terpin hydrate, m.p.119° by agitation with dilute sulphuric
acid, afforded chemical confirmation to the presence of dipentene.

As is evident from the literature survey, the isomerisa­
tion of 3-carene with organic acids as catalyst offers scope for
investigation, and in the following pages the study with salicylic
and oxalic acids are described.

Chem. (U.S.S.R), 1936, 6, 297 (see Amer. Chem. Absts. 1936, 30, 4843)
2. Bhushan and Sharma, J. Ind. Chem. Soc. (Ind. & News Ed.), 1950, 12,
No. 1, 29.
PART II-EXPERIMENTAL- ISOMERISATION OF 3-CARENE:

3-Carene:-- Indian turpentine oil (Bareilly, first quality) dried over anhydrous magnesium sulphate was carefully fractionated using Young and Thomas column which was well lagged with asbestos. Fractionation of 250 ml. of the oil was carried out during the course of 8 to 10 hours. The 169-171° cut from several such fractionations was collected and re-fractionated; the portion distilling at 169-171°/760 mm was bulked in and used as 3-carene. The physical constants of this 3-carene are compared with those in literature in Table I. (p.20).

Further, the 3-carene fraction was tested for freedom from α- and β-pinenes by hydroxylation: A mixture of 10 g. of the fraction, 190 g. of water and 10 g. of sulphuric acid (sp.gr.1.84) was shaken mechanically for a week. There was no separation of any terpin hydrate.

Salicylic acid:-- The May & Baker product was dried for 12 hours in an air oven at 110°, and cooled in a desiccator and used in the isomerisation experiment.

Oxalic acid:-- The Merck product was used as such in the hydrated condition in the isomerisation experiment.

* Unless otherwise stated it must be understood that all drying of oils mentioned in this thesis is done with anhydrous magnesium sulphate.

Table I: Properties of 3-carene.

<table>
<thead>
<tr>
<th>Property</th>
<th>3-carene</th>
<th>3-carene from Indian oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling point</td>
<td>170°/760 mm.</td>
<td>169-171°/760 mm.</td>
</tr>
<tr>
<td></td>
<td>170°/755 mm.</td>
<td></td>
</tr>
<tr>
<td>Refractive Index</td>
<td>n_D 1.4693</td>
<td>n_D 1.4693</td>
</tr>
<tr>
<td></td>
<td>n_D 1.4675</td>
<td>n_D 1.4710</td>
</tr>
<tr>
<td>Density</td>
<td>d_30 0.8586</td>
<td>d_28 0.8597</td>
</tr>
<tr>
<td>MR_D</td>
<td>44.21 (Cal.)</td>
<td>44.14</td>
</tr>
<tr>
<td>Optical Rotation</td>
<td>(a)_D + 7.69°</td>
<td>(a)_28 9.53° (10 cm tube)</td>
</tr>
<tr>
<td>m.p. of nitrosate</td>
<td>147.5°(decomp.)</td>
<td>147.5°(decomp.)</td>
</tr>
</tbody>
</table>

Isomerisation of 3-carene with salicylic acid:

**Isomerisation:** 3-Carene (170.1 g., 1.25 mole) and salicylic acid (29.67 g., 0.215 mole) were taken in a 500 ml. round-bottom flask fitted with a Liebig condenser carrying a

* Prepared according to the method of Simonsen.
1. Dupont, Ann.chim. 1924, 10 (1), 194.
calcium chloride guard tube and a thermometer, and heated in an oil bath for 49 hours at a temperature range of 140-155°. As the reaction proceeded, the acid dissolved completely in the oil, and refluxing was smooth. At the end of the period of refluxing, a fairly viscous brown liquid resulted. This was repeatedly washed with water, then just neutralised with 10% sodium hydroxide solution and finally steam distilled.

**Fractionation of the steam volatile portion:** The steam volatile portion was dried and it amounted to 85.63% on the wt. of 3-carene used. This pale yellow liquid with lemon odour had the following physical constants: $n_D^{28} 1.4805$, $d_28^{28} 0.8461$, $(a)_D^{28} 7.8\degree$ (10 cm. tube). It was carefully fractionated, using Young and Thomas column, and separated into several fractions, the yield and physical constants of which are given in Table II.

**Table II: Fractionation data of the steam volatile portion.**

<table>
<thead>
<tr>
<th>Fraction</th>
<th>b.p./760 mm.</th>
<th>% yield on the wt. of 3-carene</th>
<th>$n_D^{28}$</th>
<th>$d_28^{28}$</th>
<th>$(a)_D^{28}$ (10 cm. tube)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>170-173\degree</td>
<td>0.97</td>
<td>1.4750</td>
<td>0.8424</td>
<td>---</td>
</tr>
<tr>
<td>II</td>
<td>173-180\degree</td>
<td>52.24</td>
<td>1.4755</td>
<td>0.8424</td>
<td>+ 9.10\degree</td>
</tr>
<tr>
<td>III</td>
<td>180-182\degree</td>
<td>7.82</td>
<td>1.4925</td>
<td>0.8500</td>
<td>+ 9.01\degree</td>
</tr>
<tr>
<td>IV</td>
<td>Residue</td>
<td>19.70</td>
<td>1.4840</td>
<td>0.8274</td>
<td>+ 9.30\degree</td>
</tr>
</tbody>
</table>
The physical constants of the fractions indicated that 3-carene had undergone extensive conversion essentially into monoterpenes, and probably into cymenes, and this was investigated by chemical analysis of the several fractions.

Analysis of the fractions:

Fraction I:

Although the boiling range of the fraction included that of 3-carene, the following points, however, suggested that it might not contain this terpene:

(a) its refractive index ($n^2_D$ 1.4750) was higher than that of 3-carene ($n^2_D$ 1.4693).

(b) its density ($d^28$ 0.8424) was lower than that of 3-carene ($d^28$ 0.8587).

(c) its odour was lemon-like instead of the 'characteristic and curious, sweet odour' of 3-carene.

In order to settle definitely whether the fraction contained 3-carene an attempt was made to prepare the nitrosate corresponding to this terpene employing the method recommended by Simonsen¹.

Nitrosation:— The fraction (1.3 g.) was mixed with 0.6 ml. of glacial acetic acid and 1.1 g. of isomyl nitrite. This mixture was cooled (ice-salt) and 0.9 g. of nitric acid was added slowly with stirring. After an hour alcohol was added. There was no separation of any solid. This suggests the non-existence of 3-carene in the oil.

Tests for α-terpinene and sylvestrene:— With a view to finding out qualitatively the nature of the constituents of the fraction, the following tests were performed:

Beyer's test for α-terpinene:— To a portion of the fraction (1 ml.) was added Beckmann's chromic acid mixture (about 0.75 ml.). On shaking the mixture, there was the immediate formation of brown resinous flakes, an oxidation reaction characteristic of α-terpinene.

Wallach's test for sylvestrene:— On adding a drop of concentrated sulphuric acid to a portion of the oil (1 ml.) in acetic anhydride (3 to 4 ml.) an intense methylene blue colouration was shown, indicating the presence of sylvestrene.

As the quantity of the fraction was small, no solid derivatives corresponding to the above hydrocarbons were prepared from this fraction.

Fraction II:

Preparation of α-terpinene nitrosite:— On shaking a portion of the fraction with Beckmann's chromic acid mixture, there was immediate formation of brown resinous flakes, qualitatively indicating the presence of α-terpinene. Conclusive chemical

evidence of the presence of α-terpinene was obtained by preparing the nitrosite corresponding to this terpene by employing the method recommended by Wallach¹.

A concentrated aqueous solution containing 1 g. of sodium nitrite was added to a well-cooled mixture of 1.7 g. of the fraction, 1 ml. of glacial acetic acid and 3 ml. of water. A reddish yellow colour appeared after the nitrous acid had been completely absorbed. On inoculating the reaction mixture with a small crystal of pure α-terpinene nitrosite and triturating, reddish brown crystals separated out. This was collected, washed with petroleum ether and water and dried (0.9 g.). The product was then recrystallised thrice from alcohol and gave a m.p. 155⁰; it did not depress the m.p. of an authentic sample of α-terpinene nitrosite, thus establishing the presence of α-terpinene in the oil.

Attempts at identification of limonene (or dipentene):
The experiments performed to find out whether the oil contained any limonene (or dipentene) were; (a) nitrosation and (b) hydroxylation.

(a) Nitrosation:– Wallach’s method² was employed for this purpose. Nitric acid, 3.5 g. (sp.gr. 1.4) was added slowly to a mixture of 5 g. of the fraction, 4 ml. amyl nitrite and 2 ml.

The solution was cooled in freezing mixture (ice-salt), and stirred during addition. After keeping it for about 2 hours, alcohol was added to precipitate the nitrosate, and the reaction mixture was cooled thoroughly in freezing mixture. There was no separation of any solid, even on cooling with solid CO₂.

(b) Hydroxylation:— A mixture of the fraction (5g.), water (95g.) and sulphuric acid (5g. sp. gr. 1.94) was shaken for a week. There was no formation of any terpin hydrate.

Also, no terpin hydrate was obtained by the application of the method of Ono for the hydroxylation of dipentene to terpin hydrate on the fraction i.e., shaking of a mixture of the fraction (2g.), 40% sulphuric acid (6g.) at approximately 0° for 15 hours.

Test for phellandrene:— An attempt was made to find out the presence of phellandrene using the technique of Wallach and Gildemeister. Into a test tube was introduced first a solution of 5g. of sodium nitrite in 8 ml. water, and then a solution of 5 ml. of the fraction in 10 ml. of petroleum ether. To this was added slowly 5 ml. of glacial acetic acid, shaking the tube gently with a rotatory motion. There was no formation of any flocculent

precipitate characteristic of phellandrene at the junction of the layers, indicating thereby the absence of phellandrene in the fraction.

Identification of terpinolene: — The above-mentioned experiments showed that the fraction contained \( \alpha \)-terpinene but no limonene (or dipentene) and phellandrene. Another \( \pi \)-menthadiene that might be present in this fraction is terpinolene inspite of its boiling point \( (183-185^\circ) \) or \( 196-187^\circ \) being higher than that of the boiling range of the fraction \( (173-180^\circ) \). In justification of this assumption it may be recalled that Schindelmeiser\(^3\) has found that crude terpinene boils at \( 175-182^\circ \) and terpinolene at \( 187-190^\circ \), but mixture of the two boil at temperatures between these limits.

According to Wallach\(^4\) terpinolene yields a tetrabromide, \( 1:2:4:8 \)-tetrabromo-\( \pi \)-menthane with m.p. \( 116^\circ \). So an attempt was made to prepare this derivative of terpinolene by brominating a portion of the fraction.

Bromination: — Three ml. of the fraction was mixed with 12 ml. of petroleum ether and the mixture cooled (ice-salt). To this was added 2.5 ml. of well-cooled bromine drop-wise with stirring. After keeping the reaction mixture for 2 hours, the petroleum ether was slowly allowed to evaporate. There was no

1. Baeyer, Ber.1894,27,449.
separation of the solid tetrabromide corresponding to terpinolene; only liquid products were obtained.

This failure to obtain terpinolene tetrabromide was probably due to the α-terpinene present in the fraction. α-terpinene does not yield any crystalline di- or tetra- bromide, and this might have inhibited the crystallisation of the tetrabromide of terpinolene. Actually this was found to be the case.

Fractional destruction of α-terpinene with Beckmann's chromic acid mixture:— The capacity for α-terpinene to undergo oxidation in the cold with Beckmann's chromic acid mixture may be used to eliminate it from terpinolene since the latter compound is quite resistant against the action of this reagent in the cold.

16.9g. of the fraction was shaken intermittently in a 200 ml. separating funnel with 600 ml. of Beckmann's chromic acid mixture in 20 ml. portions. The un-reacted oil was steam distilled, dried, and it amounted to 6.8g. A portion of this un-affected oil was tested for α-terpinene with Beckmann's chromic acid mixture

2. Baeyer, Ber. 1894,27,815.
and there was no formation of any brown resinous flakes, testifying that this terpene had been completely eliminated.

**Bromination of α-terpinene-free oil.**—Preparation of terpinolene tetrabromide:—α-terpinene-free oil (4.6 g.) was mixed with petroleum ether (22 ml.), and this was cooled in freezing mixture (ice-salt). To this was added drop-wise well-cooled bromine (4 ml.) with stirring. The white solids which separated out on keeping the reaction mixture for 2 hours were immediately collected, washed with alcohol and dried (1.1 g.). This was recrystallised five times from ethyl acetate and showed a m.p. 116°, which was not depressed by admixture with an authentic sample of terpinolene tetrabromide.

**Hydrochlorination experiment—** Since the fraction responded to Wallach's test for sylvestrene, an attempt was made to prepare the dihydrochloride of sylvestrene from this fraction.

To a solution of 5 g. of the fraction in 100 ml. dry ether cooled in freezing mixture (ice-salt) dry hydrogen chloride was passed to saturation. After two days the ether was removed in vacuum and the residual brown oil was cooled in freezing mixture (ice-salt) for several hours. Only traces of solids separated out, showing that only negligible amount of sylvestrene was present in the oil. No attempt was made to separate any other hydrochlorides that might have been formed on hydrochlorination.

Identification of p- and m-Cymenes—Before describing the experiments that were performed in order to identify p- and m-cymenes in the fraction, it may not be out of place to give a brief account of the principle involved in the identification of these bensencoids.

The oxidation products of p- and m-cymenes are used to distinguish these compounds from compounds having a very similar boiling point such as terpinene and terpinolene. p- and m-Cymenes can be oxidised to terephthalic and isophthalic acid respectively. These acids sublime on heating, and are therefore best identified by conversion into dimethyl esters which possess sharp melting points.

When a mixture of p- and m-cymenes is oxidised with potassium dichromate-acetic acid solution, both these dicarboxylic acids are formed. The separation of these acids rests on their solubility features. Terephthalic acid is soluble only to the extent of 1 part in 67,000 parts of cold water; it is almost insoluble in hot water and in acetic acid. Isophthalic acid is soluble in 7,800 parts of water at 25° or in 460 parts of hot water; it is fairly easily soluble in acetic acid.

The identification of p- and m-cymenes by oxidation to terephthalic and isophthalic acid respectively has been consistently adopted so far as this thesis is concerned.

3. Huntress and Mulliken, ibid, p.177.
Hence, after oxidation, dilution of the reaction mixture with water thrown down completely the terephthalic acid together with some isophthalic acid. The solids separated are collected by filtration, and repeated washing with hot water (70 to 80°) dissolved the adhering isophthalic acid. The unaffected portion is identified as terephthalic acid.

The isolation of the isophthalic acid from the filtrate is done by concentrating the latter on a water bath. The solids that appear on cooling are collected and washed free of inorganic salts with cold water, and recrystallised from minimum quantity of hot water and identified as isophthalic acid.

Before oxidising a portion of the fraction, it is necessary to eliminate the unsaturates present. For example, terpinene and terpinolene can undergo conversion into p-cymene, and then into terephthalic acid during oxidation; and it is quite possible that m-menthadienes that are present can suffer a similar transformation into m-cymene and then into isophthalic acid.

**Oxidation:** Unsaturates in a portion of the fraction (4.22 g.) were destroyed by shaking for 6 hours with 10 ml. of 80% sulphuric acid. The unaffected oil was repeatedly washed with water, then with 10% sodium hydroxide solution, and finally steam distilled. The yield of the steam volatile oil after drying

amended to 0.84 g, and had $^{29}D$ 1.4870 and pale yellow colour.

This saturated oil was tested for diolefins and mono-
olefins as follows: Dissolved 0.3 ml. of the oil in 0.6 ml. of
benzene and to this solution was added 0.15 ml. of 96% sulphuric
acid. The acid layer remained unaffected, thereby showing the
absence of diolefins and monoolefins in the oil.

Oxidised 0.4556 g. of the saturated oil by carefully
heating under reflux with a solution composed of 4.521 g. of
potassium dichromate, 15 ml. water, 20 ml. glacial acetic acid
and 10 ml. concentrated sulphuric acid for 3 hours. The reaction
mixture was cooled, and diluted with water to about 250 ml; the
solids separated were collected by filtration, repeatedly washed
with cold water, and then with hot water (70-80°) to constant
weight (after drying in an air oven at about 150° for 3 to 4 hours)
which was 116 mg. (solid A). The filtrate after separating solid
solid A was concentrated on a water bath to about 20 ml. and it was
cooled. The separated solids were collected, and washed with
minimum quantity of cold water to get rid of inorganic salts, and
finally recrystallised from hot water. The crystallised product
after it was dried at about 150° for 3 to 4 hours in an air oven,
amounted to 71 mg. (solid B).

2. Xavier, Verghese and Yeddanapalli, Current Science,
1953,22,112.
Esterification: — The esterification of solid A was carried out according to the method recommended by Huntress and Mulliken for terephthalic acid. 100 mg. of solid A gave 72 mg. of ester. The ester melted at 140–141°, alone or mixed with authentic dimethyl terephthalate.

For the esterification of solid B, the method of Smith for isophthalic acid was used. 60 mg. of solid B gave 50 mg. of ester with a m.p. and mixed m.p. with dimethyl isophthalate, 64–65°, showing that solid B was isophthalic acid.

Fraction III:

This fraction responded to Baeyer's test for α-terpinene and Wallach's test for sylvestrene (Cf.p.23). Only α-terpinene was identified via α-terpinene nitrosite using the method adopted for its identification in fraction II (Cf.p.24). A portion of this fraction (1.7 g.) yielded 0.9 g. of α-terpinene nitrosite.

Fraction IV: (Residue):

This fraction responded to Baeyer's test for α-terpinene and Wallach's test for sylvestrene (Cf.p.23). However, no attempt was made to identify these hydrocarbons by chemical means. Instead a search was made to find out whether this residue contained any terpinolene.

Preparation of terpinolene tetrabromide: Preliminary attempts to prepare the solid tetrabromide corresponding to that of terpinolene by straight bromination of a portion of the residue in petroleum ether were unsuccessful. Therefore, α-terpinene present in the residue was eliminated before bromination of the residue.

A portion of the residue (8.57 g.) was treated with Beckmann’s chromic acid mixture (60 ml.) to destroy fractionally the α-terpinene present. On steam distilling, the unaffected oil came over and after drying it amounted to 4.1 g.

α-terpinene-free oil (4 g.) was dissolved in petroleum ether (18 ml.) and the mixture cooled (ice-salt). Well-cooled bromine (3.3 ml.) was added drop-wise to the oil-petroleum ether solution with stirring. The white solids, which separated on keeping the reaction mixture for about two hours and allowing the petroleum ether to evaporate, were immediately collected, washed with alcohol and dried (730 mg.). The dried product was recrystallized five times from ethyl acetate. This gave a m.p. 116°, which was not depressed by admixture with an authentic sample of terpinolene tetrabromide.
The action of salicylic acid on 3-carene (I) leads to α-terpinene (II), terpinolene (III), p-cymene (IV), m-cymene (V), and probably to sylvestrene (VI) (?):
Isomerisation of 3-carene with oxalic acid:

Isomerisation:— 3-Carene (170.1 g., 1.25 mole) and oxalic acid (21.77 g., 0.1728 mole) were taken in a 500 ml. round-bottom flask fitted with a Liebig condenser carrying a calcium chloride guard tube and a thermometer, and heated in an oil bath for 49 hours at 124 to 135°. Within 5 to 10 minutes, the reaction mixture turned brown, and as the heating proceeded, the oil and the acid formed a homogeneous mixture. After the period of refluxing, a viscous, brown liquid was obtained. This was repeatedly washed with water, and treated with 10% sodium hydroxide solution to neutralise any acid present and finally steam distilled. The steam volatile portion was dried, and amounted to 63.2% on the wt. of 3-carene used. It had a pale yellow colour and lemon odour, and had the following physical constants: $n^\text{D}_{5} = 1.4795$, $d^\text{D}_{20} = 0.8568$ and $(\alpha)^{34}_{D} + 1.2^\circ$ (10 cm. tube).

Fractionation of the steam volatile portion:— By careful fractionation using a Young and Thomas column lagged well with asbestos, the steam volatile portion was divided into three fractions, the yield and physical constants of which are given in Table III on p.36.

The fractionation data clearly indicated that 3-carene had undergone extensive transformations to monoterpenes, and probably to cymenes. The low optical rotation of the steam volatile portions as well as of fractions II and III suggested that
Table III: Fractionation data of the steam volatile portion:

<table>
<thead>
<tr>
<th>Fraction</th>
<th>b.p./760 mm.</th>
<th>% yield on the wt. of 3-carene</th>
<th>m^34</th>
<th>d^34</th>
<th>(a)m^34 (10 cm. tube)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>169-171°</td>
<td>4.20</td>
<td>1.4710</td>
<td>0.8511</td>
<td>........................</td>
</tr>
<tr>
<td>II</td>
<td>171-180°</td>
<td>36.90</td>
<td>1.4764</td>
<td>0.8461</td>
<td>+ 1.2°</td>
</tr>
<tr>
<td>III</td>
<td>Residue</td>
<td>19.30</td>
<td>1.4935</td>
<td>0.8694</td>
<td>+ 1.1°</td>
</tr>
</tbody>
</table>

3-carene and optically active isomers of 3-carene, if present in the reaction mixture, must be in very small quantities.

Analysis of the fractions:

Fraction I:

An attempt to prepare the nitrosate corresponding to 3-carene from the fraction employing the method recommended by Simonsen was futile (Cf.p.22).

Further, the fraction responded to Baeyer's test for α-terpinene and to Wallach's test for sylvestrene (Cf.p.23).

Fraction II:

Preparation of α-terpinene nitrosite:— For this purpose, the method recommended by Ipatieff and Pines was used. A concom-

trated aqueous solution of 3.7 g. of sodium nitrite was added to a mixture of 1.7 g. of the fraction and 3.7 g. of 20% aqueous acetic acid solution. After the absorption of the liberated nitrous acid by the oil, a viscous brown oily product was obtained. On inoculating the reaction mixture with a small crystal of pure α-terpinene nitrosite, and scratching the sides of the container with a glass rod, brown red crystals were obtained. These were separated by filtration, and washed with petroleum ether and dried (0.93 g.). This was recrystallised thrice from alcohol and showed a m.p. 155°. Mixed m.p. with α-terpinene nitrosite was undepressed.

Attempts at the identification of limonene (or dipentene):—
The attempts to identify limonene (or dipentene) in the fraction by hydroxylation (Cf.p.25), bromination ¹, by treatment with Beckmann's chromic acid mixture followed by bromination or by way of mercuric acetate complex ² met with failure. It may be mentioned that the failure to obtain the mercuric acetate complex is a definite indication of the absence of limonene (or dipentene).

Test for phellandrene:— Test for the presence of phellandrene in the fraction using the technique of Wallach and Gildemeister (Cf.p.25) was negative.

1. Baeyer, Ber. 1894, 27, 448.
2. Larrue, Trabajos lab.bioguin.quim.spl. 1940,(2) I, 53; Paleato, ibid, 1940,(2) I, 121 (through Amer.Chem.Absts. 1944, 38, 2329.).
Hydrochlorination experiment:— Although the fraction responded to Wallash's test for sylvestrene, the hydrochlorination of the fraction as described in the salicylic acid experiment (Cf.p.28) gave no appreciable amount of sylvestrene dihydrochloride.

Identification of p- and m-cymenes:— Unsaturates in a portion of the fraction (9.46 g.) were destroyed by shaking 6 hours with 20 ml. of 80% sulphuric acid. The unaffected oil was separated and repeatedly washed with water, then with 10% sodium hydroxide solution and finally steam distilled. The yield of the steam volatile portion after drying amounted to 2.1 g. (mD 1.4880) and it was free from diolefins and monoolefins (Cf.p.31).

A portion of this saturated oil (0.4552 g.) was oxidised by heating under reflux with a solution composed of 4.5 g. of potassium dichromate, 10 ml. concentrated sulphuric acid, 20 ml. glacial acetic acid and 15 ml. water, for 3 hours. The yield of terephthalic acid amounted to 307 mg. and that of isophthalic acid 33.4 mg.

Fraction III:(Residue):

Preparation of α-terpinene nitrosite:— This was carried out according to the method of Ipatieff and Pines (Cf.p.36). 1.7 g. of the fraction gave 0.82 g. of α-terpinene nitrosite, which after a three-fold recrystallisation from alcohol gave a m.p. 155°;
this was not depressed by admixture with pure $\alpha$-terpinene nitrosite.

Attempts at the identification of terpinolene:—Bromination of the fraction with and without prior treatment of the fraction with Beckmann's chromic acid mixture did not give any bromo-derivative, unlike the previous observation in connection with the isomerisation by salicylic acid (Cf. p. 28).

Wallach's test for sylvestrene:—The fraction answered the $\text{Ac}_2\text{O} - \text{H}_2\text{SO}_4$ test for sylvestrene (Cf. p. 23).

Summary.

From the analytical results on the isomerisation of 3-carene (I) with oxalic acid, it may be concluded that the terpene is transformed into $\alpha$-terpinene (II), $\pi$-cymene (IV) and $\alpha$-cymene (V) accompanied probably by small amounts of sylvestrene (VI)(?):
PART III - DISCUSSION ANDREACTION MECHANISM

The object of the experiments described in Part II was to study the action of salicylic and oxalic acids on 3-carene. The research was centred on the analysis of the isomers and the aromatics formed in these reactions.

We have seen that the steam volatile portions of the salicylic and oxalic acid experiments amounted to respectively 95.63\% and 69.2\% on the wt. of 3-carene used (Cf.pp21,35). These figures included the saturates such as cymenes which were formed by secondary processes. As has been shown (Cf.pp31,39), the saturates in fraction II of the steam volatile portions in the salicylic and oxalic acid experiments amounted to respectively 10.35\% and 9.15\% on the wt. of 3-carene. Bearing in mind that 3-carene was not present in the steam volatile portions (Cf.pp22, 36), it may be assumed that the yield of the isomers amounted to roughly 75.28\% and 59.05\% on the wt. of 3-carene in the salicylic and oxalic acid experiments respectively.

With salicylic acid, 3-carene yielded the following isomers: \(\alpha\)-terpinene, terpinolene and sylvestrene (?), and with oxalic acid, \(\alpha\)-terpinene and sylvestrene (?). The absence of terpinolene in the oxalic acid experiment was striking. Further, limonene (or dipentene) and phellandrene were not formed in these isomerisations.
Complete separation of these isomers could not be
effected by fractionation\(^1\); the isomers were more or less dis-
tributed in all the fractions. Nevertheless, \(\alpha\)-terpinene was
identified via its nitrosite, \(m.p.155^\circ\) and terpinolene by pre-
paration of its tetrabromide, \(m.p.116^\circ\). Sylvestrene was tested
only qualitatively with \(\text{Ac}_2\text{O}-\text{H}_2\text{SO}_4\); it was not formed in suf-
ficient quantity for characterisation via its dihydrochloride.
Available evidence therefore indicate that the bulk of the
isomers was composed of \(p\)-menthadienes.

On the analytical side, a significant observation was
made during the identification of terpinolene as its tetrabromide
in the fractions. In presence of \(\alpha\)-terpinene, the tetrabromide
refused to crystallise out on straight bromination of the oil
(Cf.pp.26,27). Direct proof that \(\alpha\)-terpinene interfered came
from the fact that fractional destruction of this \(p\)-menthadiene
with Beckmann's chromic acid mixture followed by bromination
afforded terpinolene tetrabromide (Cf.p.29).

Coming to the saturates derived from fraction II, their
oxidation furnished terephthalic and isophthalic acids. These
dicarboxylic acids must be derived from the cymenes (\(p\)- and \(m\-
respectively) because the boiling range of fraction II included
that of the cymenes, and the saturates had refractive indices
fairly comparable to the cymenes (Cf.pp.31,32,91). Based on the
yields of the dicarboxylic acids, the saturated oil of the
salicylic acid experiment contained \(p\)- and \(m\)-cymenes equivalent
to 20.52% and 12.61% (theor.) respectively, i.e., a total of 33.13% aromatics, and the saturated oil of the oxalic acid experiment contained p- and m-cymenes equivalent to 54.45% and 5.92% (theor.), i.e., a total of 60.37% aromatics.

Although the cymenes formed constituted a very small proportion of the steam volatile oils, the preponderance of p-cymene over m-cymene was significant. With salicylic acid, the approximate ratio of p- to m-cymene was 3:2; and with oxalic acid, 9:1. Hitherto, only p-cymene has been reported during the isomerisation of 3-carene (Cf. p. 16). So the formation of both the cymenes in the present investigation is a new observation.

The method of analysis of p- and m-cymenes in a mixture calls forth some comment. It is a new and simple method based on the oxidation of p- and m-cymenes into terephthalic and isophthalic acids respectively and separation of the dicarboxylic acids from one another by extraction with water. The dicarboxylic acids are identified via their respective dimethyl esters. The reliability of the method has been amply verified by analysis of cymene mixtures in the aromatisation studies on 3-carene described in the sequel (Cf. Section C, Part V).

An immediate general observation regarding these isomerisation reactions is that the cyclopropane ring of 3-carene must have suffered fission at the C₆-C₇ and C₄-C₇ bonds to form
p- and m- derivatives respectively. The carbon framework of 3-carene (VII) and of the p- and m- hydrocarbons (VIII and IX), as well as the mode of fission of the C-C linkages are represented in the following scheme:

![Diagram of carbon frameworks](image)

**Stereochmical considerations:**

From a consideration of the stereochemistry of cyclohexane derivatives and on the basis of the dichotomy of cycle-hexane bonds, 3-carene can be represented as follows:

![Stereoisomers](image)

1. For references see Barton, J. Chem. Soc. 1953, 1027.
In the cis-isomer, of the two bonds exterior to the nucleus of the cyclohexane ring which form the cyclopropene ring, one is equatorial and the other polar, and in the trans-isomer, both these bonds would be equatorial. Now if the cis-variety is fissioned, it can give rise to only $\alpha$-menthadienes because the conformation adopted by a substituted cyclohexane is, in general that with the maximum number of equatorial substituents. But the trans-isomer is expected to undergo fission either way because both will give rise to cyclohexane system with an equatorial substitution.

From the experimental observation it appears that the 3-carene consists of a mixture of trans- and cis-isomers in which the former predominates. This is in conformity with the observation of Simonsen, who obtained both trans- and cis-caronic acids by oxidative degradation of 3-carene.

**Reaction Mechanism:**

As regards a detailed mechanism of these conversions, the only attempts at such mechanisms for the isomerisation of 3-carene are by Lyubarski, Brooks, and Bhushan and Sharma.

1. For summarising article see Hassel, Research, 1950, 2, 504.
3. Lyubarski, Zhur Prikladnoi Khim, 1931, 4, 361; (Amer. Chem. Absts., 1932, 26, 717)
5. Bhushan and Sharma, ref.(2) p.16.
Lyubarskii's scheme suggests the possible conversion of 3-carene into dipentene and sylvestrene through the intermediate p-terpinolene and m-terpinolene respectively:

\[
\begin{align*}
\text{3-Carene} & \quad \rightarrow \quad \text{p-Terpinolene} \quad \rightarrow \quad \text{Dipentene} \\
\text{m-Terpinolene} & \quad \rightarrow \quad \text{Sylvestrene}
\end{align*}
\]

Now it may be pointed out that p-terpinolene has not been converted into dipentene to date. Wallach\(^1\) has shown that the exocyclic double bond in this p-menthadiene wanders into the ring to give \(\alpha\)- and \(\gamma\)-terpinenes, and not within the side-chain to give dipentene. A similar shift can be anticipated for m-terpinolene, thus ruling out the possibility of the formation of sylvestrene.

Further, the above scheme envisages only four realisable isomers from 3-carene. Actually this is not the case. For instance, \(\alpha\)- and \(\gamma\)-terpinenes have been obtained by isomerising 3-carene (Cf.pp.16,17).

Since no experimental conditions can be gathered from Lyubarskii's scheme, seen only in abstract, this scheme need not be examined further.

Brooks suggests that the initial isomer arising from 3-carene (I) by decyclisation of its labile ring would be $\alpha$-phellandrene (X):

\[
\text{I} \quad \rightarrow \quad \text{X}
\]

This is untenable for the following reasons:

Firstly, 3-carene has not been isomerised into $\alpha$-phellandrene so far.

Secondly, the initial isomerisation of 3-carene into $\alpha$-phellandrene implies that decyclisation of 3-carene has taken place only at the C$_6$-C$_7$ bond, and hence p-derivatives are the sole products derivable from 3-carene. This is not in conformity with experimental observations. For instance, we have seen that m-symene and sylvestrene (?) are obtainable from 3-carene along with p-derivatives. The formation of the m-compounds implies of necessity the fission of the cyclopropane ring of 3-carene at the C$_4$-C$_7$ bond, and Brooks's scheme has no provision for their formation.

New attention may be drawn to the radical mechanism of 3-carene suggested by Bhushan and Sharma.
According to this mechanism, it is proposed that the initial rupture of the cyclopropane ring of 3-carene gives rise to free valencies, and their recombination introduces another double bond, either in the 6-membered ring or in the side-chain. The cleavage of the cyclopropane ring may occur at the C₆-C₇ or C₁-C₇ bond, indicated by the dotted arrows (I), giving rise to p- and m- compounds respectively. Moreover, it is suggested that these double bonds may induce isomeric change by further shifting of their positions, a property characteristic of cycloolefins. Of the p-series, α-terpinene (XI), α-terpinene (II) and dipentene (XII), and of the m-series, Δ³:₆-m-menthadiene (XIII) and Δ⁶:₉(9)-m-menthadiene (VI)(sylvestrene) are supposed to be the products derivable from 3-carene. These are represented in the following isomerisation scheme:
There are a few significant points in favour of this mechanism:

(1) The cyclopropane ring possesses many of the properties associated with the ethylenic double bond. The formation of \( \gamma \)-terpinene or of \( \Delta^2 \)-menthadiene by decyclisation of 3-carene logically follows from this. Such a transformation is similar to the conversion of carone (XIV) into carvenone (XV), the essential change being a change from a cyclopropane ring to a double bond, and is more acceptable than the initial formation of \( \pi \)- and \( \pi \)-terpinolene as suggested by Lyubarskii, or of \( \alpha \)-phellandrene as suggested by Brooks.

![Diagram](image)

(2) The shifting of the double bonds from the isolated positions as in \( \gamma \)-terpinene to the conjugated positions as in \( \alpha \)-terpinene is a generally admitted possibility since it leads to a more stable compound, and

(3) The formation of dipentene and sylvestrene is a direct consequence of the two-directional rupture of the cyclopropane ring.

The reaction mechanisms just considered show that there is no unanimity as to the initial products that are formed by the scission of the cyclopropane ring of 3-carene. In the p-series, p-terpinolene, α-phellandrene, α-terpinene and dipentene, and in the m-series, m-terpinolene, sylvestrene and \( \Delta^3:6 \)-\( \Delta \)-menthadiene have all been suggested to be formed as a direct consequence of the cleavage of the cyclopropane ring. The various ethylenic linkages arising from the two-directional rupture of the cyclopropane ring of 3-carene are epitomised in the hypothetical 'structures' (XVI) and (XVII), wherein the double bonds formed are indicated by dotted lines:

An alternative mechanism is therefore proposed here to explain the formation of the variety of products obtained in the isomerisation of 3-carene with salicylic and oxalic acids.

**Carbonium Ion Mechanism:**

It has been claimed\(^1\) that many of the hydrocarbon reactions catalysed by acid-type catalysts can be explained by

\* A detailed discussion of the carbonium ion mechanism of terpenoid reactions is deferred to Section G.

the carbonium ion theory of Whitmore\textsuperscript{1,2}. Attempt is here made to explain the reactions of 3-carene catalysed salicylic and oxalic acids (Cf. previous part) on the basis of the initial formation of carbonium ions and the subsequent reactions they undergo to give the observed products.

The essential features of these acid catalysed hydrocarbon reactions are the production of carbonium ions and the general reactions they can undergo according to specific rules. Two of the methods of formation of carbonium ions and the pertinent reactions of carbonium ions are outlined hereunder.

Formation of carbonium ions:

(a) \textit{From olefins}\textsuperscript{1,2}:- Acids convert olefins to carbonium ions by addition of protons from the acids to the extra pair of electrons in the double bond (the \( \pi \) electrons):

\[
\begin{align*}
\overset{\cdot}{C} : \overset{\cdot}{C} + H^+ & \rightleftharpoons \overset{\cdot}{C} : \overset{\cdot}{C} \\
\end{align*}
\]

(b) \textit{From cyclopropanes}\textsuperscript{3}:- Acids convert cyclopropanes to carbonium ions by cleavage of the ring with acceptance of

\begin{enumerate}
\item Whitmore, J.Amer.Chem.Soc.1932,54,3274.
\item Schmerling, Ind.Eng.Chem.1953,45,1452.
\end{enumerate}
protons from the asides:

\[
\begin{align*}
\text{CH}_2 & \quad + \quad \text{H}^+ \quad \overset{\text{eq}}{\leftrightarrow} \quad \text{CH}_3-\text{CH}_2-\text{CH}_2^+ \\
\text{CH}_2 & \quad \text{CH}_2 \\
\end{align*}
\]

Reactions of carbonium ions:

The carbonium ion formed by one of the processes just considered, is capable of undergoing several types of reactions. This is because the carbonium ion carbon atom is left with only six electrons, and is therefore positively charged, and can undergo the changes which are characteristic of an atom with a deficiency of electrons. The following are the typical reaction types.

Reaction type I:- The carbonium ion (XVIII) reacts intramolecularly by attracting an electron pair connecting an \( \alpha \)-carbon to a hydrogen atom. The carbonium ion carbon atom completes its octet, and a proton is expelled. The net result is the creation of a multiple linkage, and therefore an olefin formation (XIX):

\[
\begin{align*}
\text{XVIII} & \quad \overset{\text{eq}}{\leftrightarrow} \quad \text{XIX} \\
\text{XVIII} & \quad \overset{\text{eq}}{\leftrightarrow} \quad \text{XIX} \\
\end{align*}
\]

The decomposition of a carbonium ion in the above fashion may lead to the formation of either the original olefin or a new olefin. For instance, the carbonium ion (XXI) may expel a proton either by attracting an electron pair from the C_1 carbon atom to give the original olefin (XX) or by attracting an electron pair from the C_3 carbon atom to give a new olefin (XXII):

\[ \text{CH}_2=\text{CH}_2-\text{CH}_2-\text{CH}_3 \xrightarrow{H^+} \text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3 \]

XX \quad \quad \quad \quad \quad XXI \quad \quad \quad \quad \quad XXII

**Reaction type II:** The carbonium ion can isomerise to a new carbonium ion by migration of a proton with its binding electrons (the hydride ion shift $\sim$H:). For instance, the carbonium ion (XXIII) can undergo an hydride ion shift to give a new carbonium ion (XXIV):

\[ \text{XXIII} \xrightarrow{\sim \text{H}:} \text{XXIV} \]

It will be seen that the charge after the hydride ion shift is on the atom which was once adjacent to the carbonium ion carbon atom.
Reaction type III: The carbonium ion can extract a hydride ion from a neutral molecule to form a new carbonium ion and a new molecule:

\[
\overset{\text{R}}{\overset{\text{H}}{\text{C}}} \overset{\text{C}}{\text{H}} < + : \overset{\text{R}}{\text{H}} \iff \overset{\text{H}}{\overset{\text{R}}{\text{C}}} \overset{\text{C}}{\text{H}} < + : \overset{\text{R}}{\text{H}}
\]

The Beta Rule: When a carbonium ion carbon takes a pair of electrons intramolecularly, that pair of electrons always comprises one of the bonds beta to the original carbonium ion carbon.

Application to 3-carene:

Applying the mode of formation of carbonium ion from olefins to 3-carene (I), the acceptance of a proton derived from the acid catalyst by the extra pair of electrons of the double bond, results in the carbonium ion (XXV). The carbonium ion (XXV)

\[
\begin{align*}
&\overset{\text{I}}{\text{I}} \iff \overset{\text{XXV}}{\text{XXV}} \iff \overset{\text{XXVI}}{\text{XXVI}} \iff \overset{\text{XXVII}}{\text{XXVII}}
\end{align*}
\]

can stabilise itself in two simple ways to give isomers. The C⁺ can complete its octet by appropriating an electron pair: (a) from within the Me- group directly attached to it, or (b) from a bond connecting an α-carbon (C₅) to a hydrogen atom. In either case a proton is expelled and a multiple linkage is formed. This is reaction of type I. The first mode of stabilisation leads to β-carene (XXVI), and the second to Δ⁴-carene (XXVII). To date none of these processes has been realised experimentally and therefore such deactivations of carbonium ion (XXV) may be regarded as only theoretical possibilities.

Now the C⁺ in (XXV) can attract an electron pair of the C₂-C₃ or C₅-C₆ bond in conformity with the β-bond rule. The consequence of such a step is the rupture of the 6-membered ring, leading to a new carbonium ion (XXVIII) or (XXIX), which can further stabilise by appropriate transformations. But this type of fission of the 6-membered ring of 3-carene has not been observed in any of the isomerisation studies so far.
Further, the carbonium ion (XXV) cannot lead to the isomers actually observed experimentally.

On the other hand, carbonium ions can be formed by fission of the cyclopropane ring of 3-carene with acceptance of protons, and since the fission of the 3-membered ring can occur in two ways, the following two carbonium ions (XXX) and (XXXI) may be postulated:

\[
\begin{align*}
\text{XXX} & \quad + \quad \text{H}^+ \\
\text{XXXI} & \quad + \\
\end{align*}
\]

Now carbonium ions (XXX) and (XXXI) can furnish the p- and m-menthadienes respectively generally observed in acid catalysed isomerisations of 3-carene.

Applying reaction type I, expulsion of a proton from (XXX) by appropriation of an electron pair from within the Me-group directly attached to the C⁺ results in limonene (or dipentene) (XII), and terpinolene (III) is the product arising from appropriation of an electron pair by the C⁺ from the C₄-H bond with expulsion of a proton. Terpinenes can be accounted from the carbonium ion (XXX) by applying reaction types II and I. The carbonium ion (XXX) undergoes isomerisation by an hydride
ion shift to give the carbonium ion (XXXII) which gives
α-terpinene (II) or β-terpinene (XI) by expulsion of a
proton, depending upon whether the C3-H or C5-H bond is involved.

Similarly, the m-menthadienes can be accounted for by
considering carbonium ion (XXXI). For instance, sylvestrene (VI)
is the product arising from the carbonium ion by attracting an
electron pair from within the Me- group directly attached to the
C+ with expulsion of a proton:

\[
\text{XXXI} \quad \text{VI}
\]
It has been stated that the isomers obtained from 3-carene using salicylic acid were terpinolene, α-terpinene and sylvestrene (?), and using oxalic acid, α-terpinene and sylvestrene (?). As explained in the preceding paragraphs, these p-menthadienes and sylvestrene are derivable from carbonium ions (XXX) and (XXXX) respectively.

As is evident, in both these isomerisations carbonium ion (XXX) has not decomposed in such a way as to yield limonene (or dipentene)(XXI), but instead it has yielded terpinolene (III) and α-terpinene (II) when salicylic acid was used, and α-terpinene (II) when oxalic acid was used. This shows the relative difficulty of proton elimination from carbonium ion (XXX) in favour of limonene (or dipentene) formation. The striking behaviour of oxalic acid in not yielding terpinolene from 3-carene may probably be due to its more acidic character than salicylic acid.

The absence of phellandrene in the products of isomerisations of 3-carene may be explained as follows: The carbonium ion (XXXIII) which yields by proton elimination α-phellandrene (X), could only be obtained from carbonium ion (XXX) by an isomerisation involving a two-step hydride ion shift. Carbonium ion (XXXII) is the intermediate isomer. Now, carbonium ion (XXX) can
deactivate with formation of terpinolene (III) as in the salicylic acid experiment, or it can suffer isomerisation to carbonium ion (XXXII), the latter furnishing α-terpinene (II) as observed in both the experiments. It is the residual carbonium ion (XXXII) which escaped deactivation that would serve as raw material for carbonium ion (XXXIII). Actually carbonium ion (XXXII) has completely stabilised itself by proton elimination to yield α-terpinene, thereby accounting for the absence of α-phellandrene (X) in the products.

Concerning the formation of αymenes in these isomerisation studies, it has been stated that this is the first time such aromatisations involving the two-directional fission of the cyclopropane ring of 3-carene have been observed. These aromatisations are not accompanied by evolution of hydrogen, and may therefore be the result of hydrogen transfer reactions. Although complete experimental evidence is not available to postulate a reaction mechanism, it may be accounted on the basis of the carbonium ion theory.
The essential steps leading to the formation of p-cymene (IV) are represented hereunder:

\[ \text{XXX} \xrightarrow{\sim H^+} \text{XXXII} \xleftarrow{\sim H^+} \text{II} \]

\[ \text{II} + \text{XXXII} \xleftrightarrow{\text{XXXIV}} \text{XXXIV} \]

\[ \text{XXXV} \xrightarrow{\sim H^+} \text{IV} \]
A similar mechanism would account for m-symene (V):

\[
\begin{align*}
\text{XXXI} & \xrightarrow{\text{H}^+} \text{XXXVI} \\
\text{XXXVI} + [\text{XXXVII}] & \xleftrightarrow{\text{H}^+} [\text{XXXVIII}] + \text{XXXIX}
\end{align*}
\]

Supporting evidence for this type of mechanism for the formation of p- and m-symenes is afforded by the investigations of Ipatieff and his co-workers\(^1\).

PART IV- SUMMARY OF SECTION B:

(1) For the first time, 3-carene has been isomerised using organic acids, namely, salicylic and oxalic acids.

(2) 3-Carene has been isomerised into terpinolene, \( \alpha \)-terpinene and sylvestrene (?) with salicylic acid, and into \( \alpha \)-terpinene and sylvestrene (?) with oxalic acid.

(3) The conversion of 3-carene into \( \pi \)- and \( \mu \)-mentha-dienes belongs to the class of isomerisation by 'declyclisation'.

(4) The isomerisation is accompanied by aromatisation into \( \pi \)- and \( \mu \)-cymenes. \( \pi \)-Cymene is formed in greater quantities than \( \mu \)-cymene. This type of reaction is observed for the first time in acid catalysed isomerisations of 3-carene.

(5) The isomerisation predominates over the aromatisation of the isomers formed.

(6) The formation of \( \pi \)- and \( \mu \)- compounds from 3-carene definitely establishes that the cyclopropane ring of the latter has undergone two-directional rupture at the \( C_6-C_7 \) and \( C_6-C_7 \) linkages.

(7) The two-directional fission of 3-carene to yield \( \pi \)- and \( \mu \)-compounds has been explained by stereochemical considerations.

(8) Terpinolene has been identified in the presence of \( \alpha \)-terpinene by fractional destruction of the latter with Beckmann's chromic acid mixture and brominating the unaffected oil.
(9) A method has been developed for identifying p- and m-xylene in a mixture by oxidation to terephthalic and isophthalic acids respectively, separating the acids from one another by extraction with water, and identifying them by conversion into dimethyl esters.