SECTION C.

LIQUID PHASE AROMATISATION OF 3-CARENE INTO PARA- AND META- CYMENES.

It is proposed to deal with in this section:

Part I: p-Cymene - methods of production
Part II: m-Cymene - methods of production
Part III: Purification of p- and m-cymenes
Part IV: Identification and estimation of p- and m-cymenes.
Part V: Experimental and discussion and Part VI: Summary.

PART I-p-CYMBNE - METHODS OF PRODUCTION:

p-Cymene occurs in numerous volatile oils—for example, in Swedish and Russian turpentine oil, in oil of lemon, sage, thyme, origanum, savory, coriander, ajowan, angelica, cumin, olibanum, nutmeg, star anise, cinnamon, etc.¹

The chief constituent of sulfite turpentine, a by-product of wood pulping process, is p-cymene, ranging from 70 to 90%.² The recovery of p-cymene during sulfite cooking is a well-known process. During World War I, a considerable amount of

This material was recovered to manufacture toluene and related compounds. However, this was not the case in World War II. In the sulfite mills in Germany, Norway, Sweden and Finland, in the summer of 1945, there was no indication of any recovery of this material. It also appears that p-cymene has never been recovered on other than an experimental scale in the United States.

A Committee of the Canadian Pulp and Paper Association to investigate the availability of p-cymene in Canada found that due to the methods of heat recovery from the waste liquor in use in modern mills and to the resulting extremely low yield of p-cymene, the production of this chemical from sulfite waste liquor was uneconomical.

It follows therefore that one has to depend on other sources for p-cymene. There are a few methods for the production of p-cymene using toluene as raw material, but these methods are not economically viable.

1. Private Communication of Allan C. Hill, Gaspesia Sulfite Co Ltd., Chandler, Quebec.
do not seem to have been used industrially. This is probably because in these methods (except in the case of propylation of toluene using 96% H$_2$SO$_4$), the conversion to p-eymene is not satisfactory; m- and o-eymenes are also formed, and the separation of p-eymene from these isomers in a state of purity is difficult.

A perusal of literature shows that a variety of terpenoids, and essential and 'synthetic' oils containing these substances in different proportions and combinations, summarised in Table I, (p.66) have been converted into p-eymene, of which the asterik marked materials constitute the starting point for the industrial production of p-eymene.

For successful aromatisation of the terpenoids given in Table I, the essential pre-requisite is that they must possess the p-eymene carbon framework as in the case of the monocyclic terpenoids, or attain it by (a) fission of the less thermodynamically stable ring as in the case of the bicyclic terpenoids and (b) ring closure as in the case of the acyclic terpenoids. These considerations would be clear by reference to fig.1 (p.67) in which is given (i) the structure of (a) p-eymene (I), (b) typical

1. Ipatieff et al, ref.(6), p.64.
2. Berry and Read, ref.(7), p.64.
Table I: Terpenoids Aromatised into p-sylvene

<table>
<thead>
<tr>
<th>Kind</th>
<th>Nature</th>
<th>System</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\alpha)-pinene*, (\beta)-pinene, (\delta)-carene*, (\alpha)-thujene, verbenene, pinane, earane and samphene.</td>
<td>Hydrocarbon</td>
<td>Bicyclic</td>
</tr>
<tr>
<td>(\alpha)-terpinene*, (\beta)-terpinene, limonene*, dipentene*, terpinolene*, (\alpha)-phellandrene, p-3-menthene, p-menthane* and menogerene.</td>
<td>Hydrocarbon</td>
<td>Monocyclic</td>
</tr>
<tr>
<td>Allo-oceanine</td>
<td>Hydrocarbon</td>
<td>Acyclic</td>
</tr>
<tr>
<td>Verbenol, pinoarvicol and sabinol</td>
<td>Alcohol</td>
<td>Bicyclic</td>
</tr>
<tr>
<td>Terpineol ( (\alpha)-* and commercial) and menthol.</td>
<td>Alcohol</td>
<td>Monocyclic</td>
</tr>
<tr>
<td>Linalool</td>
<td>Alcohol</td>
<td>Acyclic</td>
</tr>
<tr>
<td>Thujone, umbellulone and samphor*</td>
<td>Ketone</td>
<td>Bicyclic</td>
</tr>
<tr>
<td>Menthone</td>
<td>Ketone</td>
<td>Monocyclic</td>
</tr>
<tr>
<td>Citral*</td>
<td>Aldehyde</td>
<td>Acyclic</td>
</tr>
<tr>
<td>Cineole</td>
<td>Anhydride</td>
<td>'Bicyclic'</td>
</tr>
<tr>
<td>Turpentine oil*, sulphate turpentine*, pine needle oil*, oil essences, 'Borneol oil' and pine oil*.</td>
<td>Mixture of terpenoids</td>
<td>........</td>
</tr>
</tbody>
</table>

* This list includes the terpenoids aromatised in the liquid and vapour phases.
Figure I: Structural relationship of terpenoids to p-eynene.

monocyclic terpenoids, such as dipentene (II), terpinolene (III) and \( \alpha \)-terpinene (IV), (e) typical bicyclic terpenoids such as \( \alpha \)-pinene (V), 3-carene (VI) and camphor (VII) and (d) typical acyclic terpenoids such as citral (VIII) and linalool (IX) and (ii) the mode of fission of the bicyclic terpenoids and of ring closure of the acyclic terpenoids by dotted lines, in order to attain the p-eynene carbon framework.
The literature on the aromatisation of the terpenoids summarised in Table I is voluminous. The available methods can be divided into two broad divisions, viz., liquid phase methods and vapour phase methods. However, we shall confine ourselves, in these pages, to only the most important methods of production of p-cymene in the liquid phase.

**Liquid phase aromatisation of terpenoids to p-cymene:**

**Aromatisation with Halogens:**

(a) *Iodine*: Of the bicyclic terpenoids, the aromatisation of α-pinene to p-cymene with iodine has been studied fairly extensively\(^1\). The reaction proceeds in a somewhat complex manner. The products formed are very unstable, decomposing readily with formation of p-cymene.

Another bicyclic terpenoid that has been transformed into p-cymene with iodine is thujone\(^2\).

Results of considerable interest have been obtained from a study of the iodine catalysed aromatisation of terpenes by

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1. Deville, Ann.1841,37,191; Kekule and Bruylants, Ber.1873,6,437; Oppenheim, ibid.1874,7,625; Preis and Rayman, ibid.1879,12, 1358; Denaro and Searlato, Gazzetta, 1903,33,393.

Ipatieff and his co-workers\(^1,2\). Expressed in general terms, monocyclic terpenes containing a pair of double bonds in the molecule undergo hydrogen transfer during distillation with iodine, to give cyclic monoolefins and p-cymene according to the equation \(2 \text{C}_{10}\text{H}_{16} \rightarrow \text{C}_{10}\text{H}_{18} + \text{C}_{10}\text{H}_{14}\).

Of the open chain terpenes, citral yields about 69% p-cymene on distillation with small amounts of iodine\(^3\).

(b) Bromine:– The early experiments of Deville\(^4\), Oppenheim\(^5\), Barbier\(^6\) and Kekule\(^7\) on the bromination of \(\alpha\)-pinene did not lead to the separation of any crystalline derivatives, but the isolation of p-cymene either by direct distillation or after treatment with bases was of fundamental theoretical importance in showing the relationship of \(\alpha\)-pinene to the aromatic hydrocarbons\(^8\).

p-Cymene is prepared from α-pinene in 50% yield by bromination at -18 to -15° and dehydrohalogenation of the fraction, b.p. below 195° of the product by heating with 2% iodine. Without the aid of iodine, the yield was only 35%. Formation of p-cymene from monocyclic terpenes on bromination is not unusual. For instance, α-phellandrene on treatment with bromine yields considerable quantity of p-cymene.

There had been, however, attempts by early investigators to aromatise various monocyclic terpenoids to p-cymene via bromo-derivatives with a view to establish their structural relationship to the benzenoid hydrocarbon. It is seen from a perusal of literature, that the decomposition of the bromo-compounds has been accomplished by three methods: (1) by thermal treatment (2) by treatment with bases and (3) by step-wise reduction.

Wallach's thermal decomposition of α-terpineol dibromide (I) to p-cymene (I) may be cited as an example of the first

method of aromatisation*. The reaction may be represented by the following scheme:

the formulae within brackets being hypothetical. The aromatisation is effected partly by elimination of HBr and partly by elimination of H₂O, and only 2 atoms of bromine are required.

The conversion of terpinolene tetrabromide to p-cymene by alkali treatment is an example of the second method¹.

The third method, which is of very wide application, developed by Baeyer and Villiger², consists in subjecting the terpene to exhaustive bromination, followed by removal of hydrogen bromide by step-wise reduction. The essential steps, as regards the conversion of d-limonene into p-cymene by this method are given on page 72.

* Simonsen (The Terpenes', Cambridge University Press, 2nd Edn. 1947, Vol. I, p.262) considers this conversion as an example of the method introduced by Baeyer and Villiger² for dehydrogenation of cyclic bodies by exhaustive bromination).

More important, but still little investigated of the three methods is the application of the thermal decomposition of bromo-derivatives of terpenoids to p-cymene. Essentially, this method is based on the fact that under certain conditions, bromine forms, at relatively low temperatures, high-boiling brominated products, which, because of their heat lability, can be broken down to the aromatic hydrocarbons directly without the application of any reducing agent.

Historically, this method has been utilised for the aromatisation of terpenoids to p-cymene. As mentioned earlier, Wallach's conversion of \( \alpha \)-terpineol to p-cymene via the dibromide belongs to this type of aromatisation. Again, another instance is provided by Oppenheim who converted \( \alpha \)-pinene into p-cymene by addition of two atoms of bromine followed by thermal treatment.

But it was Olsen who established the fact that the thermal method

is superior to Baeyer-Villiger method. The latter method is attended with preparative difficulties; further, it requires a process of step-wise reduction of the per-brominated derivatives. These differences become clear from the examples of the aromatisation of dl- and d-limonene by the thermal and the Baeyer-Villiger methods respectively\(^1,2\).

The aromatisation of dl-limonene by the thermal method involves the preparation of the tetrabromide (XIV) followed by the decomposition of the latter to p-cymene (I) by heat treatment. The decomposition consists in the elimination of 3 moles of HBr and the simultaneous reductive elimination of the remaining Br atom with the liberated HBr. These changes can be expressed by the following equations, wherein the compounds within the brackets are merely hypothetical:

\[
\begin{align*}
&\text{XIV} \quad \text{XVI} \\
&\quad \quad \text{H}8_r \\
\end{align*}
\]

In contrast to this method, the conversion of d-limonene to p-cymene by the exhaustive bromination method (Cf.p.72) requires

the rather difficult preparation of the perbrominated derivative, \(C_{10}H_{13}Br_7\), (XIV). The spontaneous cleavage of 3 moles of HBr from this compound would still leave 4 Br atoms, which are then eliminated by treatment with appropriate reducing agent.

It is therefore clear that for the aromatization by the bromine dehydrogenation technique, there is no need to prepare the 'fully' brominated derivatives; in other words, it is incomplete bromination which offers a guarantee to successful aromatization.

(e) Chlorine:- By passing chlorine into \(\alpha\)-pinene containing \(\text{PCl}_3\), Naudin\(^1\) obtained p-cymene in 75\% yield. According to Bert\(^2\) this method yielded only traces of p-cymene. However, Schindelmeiser\(^3\) had confirmed the observations of Naudin.

Recently, it was reported\(^4\) that chlorination of \(\alpha\)-pinene in the presence of 100\% excess of \(\text{NaHCO}_3\) gave a fraction, b.p/13 mm. 67\(^\circ\) which on agitation with ice-cold sulphuric acid gave pure p-cymene.

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2. Bert, ibid, 1923, 23, 757.
Some of the earliest patents\(^1\)-\(^4\) on the production of p-cymene from terpenes employed chlorine as the aromatising agent.

**Aromatisation with Sulphur:**

On the basis of thermodynamical calculations, sulphur is not a particularly effective dehydrogenating agent\(^5\). However, a perusal of literature shows, that a number of terpenoids such as α-pinene\(^6\), β-caryophyllene\(^7\), emaphene\(^8\), limonene\(^9\)-\(^11\), α-terpinene\(^12\), γ-terpinene\(^13\), α-phellandrene\(^14\), terpinolene\(^14\), α-terpineol\(^15\), terpineol (commercial)\(^16\), terpinyl acetate\(^15\), eucalyptol\(^16\), menthene\(^6\), linalool\(^15\), linalyl acetate\(^15\), etc., have been aromatised into p-cymene by heating with sulphur, alone or with promoters.

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5. Vesterberg and Braun, Ber.1932,65,1473.
15. Nakatsuchi, ibid.1932,25,376 B.
It cannot be said with certainty in what way sulphur acts as an aromatising agent in these dehydrogenations. Linstead\textsuperscript{1} is of opinion that dehydrogenation with sulphur presumably involves (1) addition of the reagent to an unsaturated centre followed by (2) elimination of hydrogen sulfide. In fact Sehindelaeiser\textsuperscript{2} has obtained by treating terpinene or dipentene with sulphur, compounds 'similar enough' to the peroxides of the terpenes. Under the influence of heat these compounds are split to form p-eymene and hydrogen sulfide. According to Farmer\textsuperscript{3}, sulphur can probably function as a hydrogen acceptor by a direct mechanism.

**Aromatisation under Pressure:**

Various terpenoids have been aromatised into p-eymene by digestion under pressure at temperatures of 100-500° with the following materials: (1) AlCl\textsubscript{3}, AlBr\textsubscript{3} or ZnCl\textsubscript{2}\textsuperscript{4} (2) active C\textsubscript{5} (3) solution containing SO\textsubscript{2}, CaO and S\textsubscript{6} (4) aq. solution up to 5% of (a) salts like FeCl\textsubscript{3}, AlCl\textsubscript{3}, ZnCl\textsubscript{2}, MgCl\textsubscript{2} or NaHSO\textsubscript{4} or (b) oxygen-

\textsuperscript{1} Linstead, Chemical Society Annual Reports, 1936, XXXIII, p.312.
\textsuperscript{2} Sehindelaeiser, ref.(10), p.75.
\textsuperscript{3} Farmer, Trans.Far.Soc. 1942, 345.
containing mineral acids like \( \text{H}_3\text{PO}_4 \) finally dispersed porous mixture of silicic acid with one or more of the following metals, or their oxides or sulfides: Ni, Co and Cu\(^3\) (6) Ni and Pt\(^4\) and (7) \( \text{H}_2\text{O}_5 \).

**Hydrogen transfer method**:

A reported industrial method for the catalytic disproportionation of any monocyclic terpene at atmospheric pressure makes use of a copper-nickel formate catalyst\(^6-10\). The reaction may be represented by the general equation \( \text{C}_{10}\text{H}_{16} \) (terpene) \( \rightarrow \)

\[ 2 \text{C}_{10}\text{H}_{14} \text{ (p-symene)} + \text{C}_{10}\text{H}_{20} \text{ (p-menthane)}. \]

Practically 100% theoretical yield is claimed. By careful vacuum fractionation, the reaction products can be completely separated. The method is easy, cheap and efficient, and ranks as the most outstanding in the liquid phase conversion of terpenes to p-symene.

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The catalytic disproportionation of limonene and pinene using Pt-charcoal is another notable contribution in this field. When pure limonene is boiled with Pt-charcoal, no hydrogen is evolved, but the unsaturated activity is lost. The product formed at 140° is shown to be a mixture of p-cymene and p-menthane in the approximate ratio 2 to 0.9. This agrees with the ratio demanded by the disproportionation equation, $3 \text{C}_{10}\text{H}_{16} (\text{limonene}) \rightarrow 2 \text{C}_{10}\text{H}_{14} (\text{p-cymene}) + \text{C}_{10}\text{H}_{20} (\text{p-menthane})$.

When α-pinene (V) is boiled at 156° with Pt-charcoal, it does not lose hydrogen, but passes completely into a mixture of p-cymene (I) and pinane (XVII). These are formed in approximately equimolecular proportion as required by the equation:

\[
\text{V} \quad \rightarrow \quad \text{XVI} + \quad \text{I}
\]

Only the 6:7 and not the 4:7 bond was broken in the dehydrogenation, forLeu-cymene could not be detected in the product.

Ipatieff and his co-workers studied a set of hydrogen transfer reactions embracing monocyclic terpenes having rings with

2. Ipatieff et al, refs. (1) and (2), p.69.
6 carbon atoms and 2 double bonds. Catalysts utilisable are the halogens, hydrogen halides, halohydrocarbons, halogenated carboxylic acids and acyl halides. Iodine is particularly applicable. The transformation is generally effected by heating the reactants at atmospheric pressure, and may be represented as

\[ 2 \text{C}_{10}\text{H}_{16} (\text{terpene}) \rightarrow \text{C}_{10}\text{H}_{14} (\text{p-symene}) + \text{C}_{10}\text{H}_{18} (\text{monosycloolefin}). \]

The yield of the aromatic compound ranged from 3 to 49%.

Another ingenious method of disproportionation of terpenes containing 2 double bonds e.g., terpinene, limonene, into 1 aromatic mole and 1 monosycloolefinic mole has been effected under pressure in contact with materials such as 0 to 5% aqueous solution of (a) salts like \( \text{AlCl}_3, \text{FeCl}_3, \text{ZnCl}_2, \text{MgCl}_2 \) or \( \text{NaHSO}_4 \) or (b) oxygen-containing mineral acids like \( \text{H}_2\text{PO}_4 \).

Other noteworthy examples of disproportionation are of 1-\( \alpha \)-phellandrene and d-limonene on nickel and palladised barium catalyst respectively.

In the accompanying Table II, other types of aromatisation are given.

1. Ipatieff and Pines, refs. (1) and (2) p.77.
3. Eschinazi and Bergmann, J.Amer.Chem.Soc. 1950, 72, 5651.
<table>
<thead>
<tr>
<th>Terpenoid</th>
<th>Aromatising agent</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sabinol</td>
<td>Halogen acids.</td>
<td>Fromm, Ber.1899, 21, 2030; 1900, 33, 1208.</td>
</tr>
</tbody>
</table>

**Aromatisation with Fuller's Earth.**

<p>| α-pinene | Fuller's earth | Venable, J.Amer.Chem.Soc.1923, 45, 727. |</p>
<table>
<thead>
<tr>
<th>Terpenoid</th>
<th>Aromatising agent.</th>
<th>References.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Citral</td>
<td>Fuller's earth</td>
<td>Bennett and Fraser, U.S.Pat. 1933, 1,893,879.</td>
</tr>
<tr>
<td>Pine oil</td>
<td>— do —</td>
<td>Humphrey, U.S.Pat.1933, 1,893,802 (Amer.Chem.Absts.1933,27,2164)</td>
</tr>
</tbody>
</table>

**Aromatisation with Maleic Anhydride.**

| α-terpinene     | — do —             |                                                                         |

**Aromatisation with Selenium Dioxide.**


**Aromatisation with Japanese acid clay.**

<p>| Terpineol and | — do —             | Ono, Mem.Coll.Sei.Kyoto,1925,2 (A) 153 (British Absts.1926, A 72) |</p>
<table>
<thead>
<tr>
<th>Terpenoid</th>
<th>Aromatising agent</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Camphor</td>
<td>Phosphorus pentoxide</td>
<td>Dumais and Peligot, Compt. rend. 1836, 4, 496; Kekule and Pott, Ber. 1869, 2, 121; Fittig, Ann. 1874, 172, 307; Armstrong and Miller, Ber. 1883, 16, 2259; Richter and Wolff, Ber. 1930, 62, 1721; Birch, Dean, Fidler and Lowry, J. Amer. Chem. Soc. 1949, 71, 1368.</td>
</tr>
<tr>
<td>Camphor</td>
<td>Zine chloride</td>
<td>Delalande, Ann. 1841, 38, 337.</td>
</tr>
</tbody>
</table>
PART II- m-CYMENE - METHODS OF PRODUCTION:

m-Cymene, unlike its isomer p-cymene, occurs very rarely in nature. The hydrocarbon is found in small quantities in resin essences and in Colorado shale-oil naphtha. It is also reported in Finnish wood turpentine.

Although, generally, p-cymene has been found to be the main constituent of sulfite turpentine, there is a reference in literature of the presence of m-cymene along with p-cymene in sulfite oils from Germany and Sweden. The total cymene content of these oils amounted to about 30%, but the proportion of the individual cymenes have not been reported. These are perhaps the only cases wherein both the cymenes have been found to be present concurrently in sulfite turpentine, and as such their formation merits further investigation.

Interaction of toluene with isopropyl chloride using HCl catalyst results in m-, o- and p-cymenes, of which the m-isomer constitutes approximately 22 to 27%. Another method involves the propylation of toluene in presence of AlCl₃ or BF₃, giving rise to

the three cymenes afore-mentioned, with about 29.8% of the m-

isoacen. Further, condensation of toluene with isopropyl alcohol
in presence of AlCl₃, FeCl₃ or H₂SO₄ also leads to the formation of

m-cymene³.

While a great variety of terpenoids have the p-cymene
carbon framework, relatively few terpenoids with the m-cymene carbon
framework are available. Of the terpenoids with m-cymene carbon
framework may be mentioned sylvestrene (or curvestrene) (XVIII),

2. See, Berry and Reid, ibid.1927,49,3149.
3-isopropyl- \( \Delta^{16} \)-cyclohexadiene \(^1\) (XIX), \( \alpha \)-terpinolene (XX), m-3-menthen (XXI)\(^2\), \( \Delta^{318} \)-m-menthen (XXIII), m-menthane (XXIV), sylvecarvone (XXV), sylveterpin (earveterpin) (XXVI) and dihydrecarvestrenol (XXVII). However, only sylvestrene and earvestrene have been aromatised into m-cymene by Baeyer-Villiger method\(^3\). None of these terpenoids is available in sufficient quantity for chemical processing, although sylvestrene and earvestrene might become potential raw materials, being derivable from 3- and \( \Delta^{4} \)-earene by appropriate isomerisations.

However, a terpenoid that has been repeatedly aromatised into m-cymene by dehydration with \( \text{P}_{2}\text{O}_{5} \) is fenchone (XXVIII)\(^4\)–\(^7\). This transformation essentially involves an elimination of a molecule of water from the terpenoid. But an examination of its structure shows that it possesses a carbon framework fundamentally different from that of m-cymene. The simple fission of its 5-membered ring will not lead to the carbon framework of m-cymene. Further, the ketonic function has no \( \alpha \)-hydrogen to facilitate enolisation. Hence, the aromatisation of fenchone involves extensive skeletal rearrangement and dehydration.

2. Godchot and Cauquil, Compt. rend. 1938, 206, 89.
3. Baeyer and Villiger, Ber. 1893, 21, 2057, 1898.
7. Richter and Wolff, Ber. 1930, 63, 1721.
Lacourt\(^1\) has reported m-cymene in 50% yield by dehydrating camphor-free fenchone. Richter and Wolff\(^2\) effected a similar transformation and after rigorous purification of the product, reported a yield of 164 g. of m-cymene from 630 g. of fenchone.

A reaction of unusual interest is the isomerisation of p-cymene into m-cymene (and o-cymene) by heating with AlCl\(_3\) at 100\(^\circ\)C.\(^3\)

The synthesis of m-cymene has been effected by a number of investigators, notably by Sabatier and Murat\(^4\), Pines and his co-workers\(^5\) and Bireh and his co-workers\(^6\).

Moldavkii and Kamusher\(^7\) caused the aromatisation of 2,7-dimethyl-n-octane at 450\(^\circ\) over Cr\(_2\)O\(_3\) catalyst getting an 82% yield of m-cymene. Other catalysts studied were the oxides of Zn, Al, Th and U, NiCrO\(_4\) and MoS\(_2\).

Kazanski and Plate\(^8\) also effected the aromatisation of 2,7-dimethyl-n-octane to m-cymene by passing it over Pt-charcoal catalyst, first in hydrogen and then in nitrogen.

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PART III- PURIFICATION OF p- AND m-CYMENES:

p-Cymene:-

The isolation of p-cymene in a state of purity from 'crude p-cymene' obtained by the aromatisation of terpenoids is by no means a simple operation. Only in the case of the disproportionation of p-menthadienes with copper-nickel formate catalyst has it been claimed that p-cymene is separable completely from the accompanying p-menthane by careful vacuum fractionation (Cf.p.77). This is understandable because, the disproportionation is 100% theoretical, and the fractionation involves essentially the separation of two components whose boiling points are tolerably wide apart (p-menthane: b.p.167°; for the b.p. of p-cymene see p.91).

Now a perusal of literature shows that technical or 'sulfite' cymene is invariably contaminated with unsaturates, and the isolation of pure p-cymene by fractional distillation alone is extremely difficult.¹⁻⁴

A variety of methods have been recommended for getting pure p-cymene from technical and 'sulfite' cymene.

Careful distillation followed by treatment with sulphuric acid is stated to be the best for refining p-cymene. Various concentrations and quantities of acid are recommended. Digestion with metallic sodium, phosphoric anhydride, oxidation with Beekmann's reagent or potassium permanganate, fractional distillation under reduced pressure, bromination, refluxing with sulphur, treatment with chlorosulphonic acid, percolation through silica gel, dehydrogenation over a catalyst are some of the aids to purification.

Purification of p-cymene can also be effected by its sulfonation followed by desulphonation.
Patents have been granted for refining p-cymene by treatment with condensing agents, e.g., zinc chloride¹ and hydrogen chloride².

Pure p-cymene should display no unsaturation³ or optical rotation⁴. The purity of the product can be tested with concentrated H₂SO₄ as recommended by Schorger⁵. According to this test, pure p-cymene will not colour conc. H₂SO₄. Wheeler⁶ could not confirm the test of Schorger; Karvonen⁷ and Boedtker⁸ on the other hand agree with Schorger; Karvonen explains the negative results of Wheeler as due to impurities in p-cymene, and Boedtker states that impure H₂SO₄ colours even pure p-cymene.

m-Cymene:-

Probably the most reliable method of refining m-cymene is that recommended by Richter and Wolff⁹, consisting of rigorous fractionation in vacua after treatment with concentrated sulphuric acid and finally with sodium.

¹. British and Foreign Chemical Producers Ltd., British Pat. Oct. 6, 1919, 142,738 (Amer.Chem.Absts.1920,14,2802)
⁵. Schorger, ibid. 1917,39,2672.
⁷. Karvonen, Ber. 1923,56,1824.
⁹. Richter and Wolff, Ber.1930,63,1721.
PART IV - IDENTIFICATION AND ESTIMATION OF p- AND m-CYMENES:

Identification of p- and m-cymenes:

Boiling point, refractive index and density are the important physical constants to be determined in the identification of either p- or m-cymene. The constants reported for these hydrocarbons by various investigators are summarised in Table III (p.91). It is to be noted that there is a considerable variation in the properties of cymenes reported in literature.

As regards p-cymene, it has been identified by its oxidation into terephthalic acid\(^1\), p-toluic acid\(^2\) and p-(\(\alpha\))-hydroxy-isopropyl benzoic acid\(^3\), and by its conversion into barium p-cymene sulfonate\(^4\), p-cymene sulfonamide\(^5\) and aryl benzoic acid derivative\(^6\).

## Table III: Physical constants of p- and m-cymenes.

<table>
<thead>
<tr>
<th>Source</th>
<th>Boiling point</th>
<th>Refractive index</th>
<th>Density</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>p-Cymene</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eastman Kodak Co.</td>
<td>176°</td>
<td>$n^\text{20}_D$</td>
<td>1.4395</td>
<td>Pines, Olberg and Ipatieff, J.Amer.Ch em.Soc. 1952,74,4974.</td>
</tr>
<tr>
<td>Technical</td>
<td>177.25°/760 mm</td>
<td>$n^\text{20}_D$</td>
<td>1.4909</td>
<td>Birch, Dean, Fidler and Lewry, J.Amer.Ch em.Soc. 1949,71,1368.</td>
</tr>
<tr>
<td>Technical</td>
<td>175-176°</td>
<td>$n^\text{25}_D$</td>
<td>1.4875</td>
<td>Kobe and Vittone, Ind.Eng.Chem.1940,32,775.</td>
</tr>
<tr>
<td>Camphor</td>
<td>177.10°/760 mm</td>
<td>$n^\text{20}_D$</td>
<td>1.4910</td>
<td>Birch et al, J.Amer.Ch em.Soc. 1949,71,1369.</td>
</tr>
<tr>
<td><strong>m-Cymene</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fenchone</td>
<td>175.6-175.8°/</td>
<td>$n^\text{20}_D$</td>
<td>1.4920</td>
<td>Richter and Weltz, Ber. 1930,62,1721.</td>
</tr>
<tr>
<td>760 mm.</td>
<td>4</td>
<td>$d^\text{20}$</td>
<td>0.9606</td>
<td></td>
</tr>
<tr>
<td>Fenchone</td>
<td>175.7°/758.6 mm</td>
<td>$n^\text{20}_D$</td>
<td>1.49819-</td>
<td>Lascurt, Bull.soc.chim.Belg. 1930,32,132.</td>
</tr>
<tr>
<td></td>
<td>1.49216</td>
<td>$d^\text{20}$</td>
<td>0.8626</td>
<td></td>
</tr>
<tr>
<td>2,7-dimethyl-m-</td>
<td>173-177°/</td>
<td>$n^\text{20}_D$</td>
<td>1.4920</td>
<td>Kasanski and Plate, Ber. 1936,62,1872.</td>
</tr>
<tr>
<td>octane</td>
<td>760 mm.</td>
<td>$d^\text{4}$</td>
<td>0.8600</td>
<td></td>
</tr>
</tbody>
</table>
Up till now, m-cymene has only been recognised by its oxidation into isephthalic acid\(^1\) and into m-(\(\alpha\))-hydroxyisopropyl benzoic acid\(^2\). An excellent derivative for the identification of m-cymene would be 2,4,6-trinitro-m-cymene, m.p.74.5-75\(^\circ\), recently prepared by Qvist\(^3\).

**Estimation of p- and m-cymenes:**

An interesting method for the rapid determination of small quantities of cymene in admixture with terpenes makes use of Rideal-Walker Coefficient\(^4\).

Linstead and co-workers\(^5\) have developed a semi-quantitative method for estimating p-cymene. The method consists in boiling 0.5 ml. of p-cymene with a mixture of 3.5g CrO\(_3\), 15 ml. H\(_2\)O, 15 ml. CH\(_3\)COOH and 5 ml. H\(_2\)SO\(_4\) for about 3 hours, when about 370 mg. of terephthalic acid is obtained, this yield being reproducible and not appreciably affected by increase in either indicated time of boiling or amount of CrO\(_3\). However, according to

additional data presented by the authors, about 450 mg. of p-cymene should give, under similar conditions of oxidation between 350 to 385 mg. of terephthalic acid, much less than the theoretical yield, i.e., 577 mg.

Recently, Xavier, Verghese and Yeddamapalli re-investigated this convenient analytical procedure of Linstead et al.

The method was applied to pure p-cymene (b.p. 176-176.5°/760 mm., n_D 1.4390) obtained by purifying an Eastman Kodak sample, and the results are summarised in Table IV-A (p.94), the yield of terephthalic acid for 450 mg. of p-cymene being 424 to 425 mg., a value considerably greater than the 370 mg. of Linstead et al.

Trial experiments revealed that the discrepancy between our and Linstead's results might be due to the mode of carrying out the oxidation process. If, at the start, the oxidation is made to take place vigorously, the yield of terephthalic acid is greater than the yield obtained with a mild and slow heating from the beginning, as is seen by comparing the results under A and B of Table IV. The yield of acid from slow oxidation is similar to that obtained by the other authors.

## Table IV: Oxidation of pure p-cymene to terephthalic acid

(time, 3 hours)

| CrO₃ | H₂O | H₂SO₄ | CH₃COOH | p-Cymene | Terephthalic T.im mg.per p-cymene.
<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>g.</td>
<td>ml.</td>
<td>ml.</td>
<td>ml.</td>
<td>mg.</td>
<td>acid(T) mg. 450 mg. p-cymene.</td>
</tr>
<tr>
<td>A: Rapid oxidation.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.5</td>
<td>15</td>
<td>5</td>
<td>15</td>
<td>406</td>
<td>383</td>
</tr>
<tr>
<td>3.5</td>
<td>15</td>
<td>5</td>
<td>15</td>
<td>397</td>
<td>375</td>
</tr>
<tr>
<td>4.0</td>
<td>15</td>
<td>5</td>
<td>15</td>
<td>369</td>
<td>349</td>
</tr>
<tr>
<td>B: Slow oxidation.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.5</td>
<td>15</td>
<td>5</td>
<td>15</td>
<td>399</td>
<td>319</td>
</tr>
<tr>
<td>3.5</td>
<td>15</td>
<td>5</td>
<td>15</td>
<td>386</td>
<td>310</td>
</tr>
<tr>
<td>3.5</td>
<td>15</td>
<td>5</td>
<td>15</td>
<td>361</td>
<td>314</td>
</tr>
<tr>
<td>C: Rapid oxidation.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.5</td>
<td>15</td>
<td>10</td>
<td>20</td>
<td>413</td>
<td>435</td>
</tr>
<tr>
<td>3.5</td>
<td>15</td>
<td>10</td>
<td>20</td>
<td>390</td>
<td>411</td>
</tr>
<tr>
<td>D: Rapid oxidation.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.0</td>
<td>15</td>
<td>10</td>
<td>20</td>
<td>416</td>
<td>440</td>
</tr>
<tr>
<td>3.0</td>
<td>15</td>
<td>10</td>
<td>20</td>
<td>420</td>
<td>447</td>
</tr>
<tr>
<td>3.0</td>
<td>15</td>
<td>10</td>
<td>20</td>
<td>401</td>
<td>419</td>
</tr>
</tbody>
</table>
Induced by these findings, attempt was made to evaluate the effect of changing the relative proportions of sulphuric and acetic acids on the yield of terephthalic acid from p-cymene under rapid oxidation conditions, and the results are presented in Table IV-C. The yield is now pushed up to about 474 mg. from 450 mg. of p-cymene.

On replacing CrO₃ by the more readily available and less hygroscopic potassium dichromate, rapid oxidation of p-cymene gave yields of terephthalic acid listed in Table IV-D in which column I represents the CrO₃ equivalent of the dichromate used. The average yield from 3 experiments is 475 mg. in good agreement with the yield of 474-475 mg. obtained with CrO₃ (Cf. Table IV-C).

It may be concluded that 450 mg. of pure p-cymene should, on rapid oxidation with CrO₃ give about 424-425 mg. of terephthalic acid with the acid mixture indicated in A of Table IV, and about 474-475 mg. with the higher acid mixture of C in Table IV. The latter yield can also be obtained with potassium dichromate as indicated by D of the same table.

Returning to other methods of estimating p-cymene, mention may be made of the extraction of the hydrocarbon with sulphuric acid containing 15% SO₃.

Further, there are physical methods based on ultraviolet\textsuperscript{1} and infra-red absorption\textsuperscript{2-5}, specific dispersion\textsuperscript{1}, Raman spectrum\textsuperscript{4}, and refractive index\textsuperscript{6}.

As regards \textit{m}-cymene, no chemical method is at present available for its estimation. Of the physical methods available mention may be made of the infra-red\textsuperscript{4,5} and Raman spectral analysis\textsuperscript{4}.

From the literature survey on the aromatisation of terpenoids to \textit{p}- and \textit{m}-cymenes, we find that very little work has been done on \textit{3}-carene. Guha et al\textsuperscript{6} aromatised this terpene using sulphur in conjunction with promoters such as zinc chloride, activated charcoal and diphenylurea. \textit{p}-Cymene is the sole aromatic reported in this study. This is rather surprising because \textit{3}-carene can yield both \textit{p}- and \textit{m}-cymenes by cleavage of its cyclopropane ring two-directionally at the C\textsubscript{6}-C\textsubscript{7} and C\textsubscript{1}-C\textsubscript{7} linkages respectively, as has been shown in the isomerisation experiments. It seemed to be of interest therefore to investigate in detail the two-way aromatisation of \textit{3}-carene and in the following pages experiments are described wherein this type of transformation has been achieved in the liquid phase.

PART V- EXPERIMENTAL AND DISCUSSION:

(I) Aromatisation of 3-carene with Iodine:

Experiment I:- 3-Carene (21.47 g., 0.1578 mole) was taken in a round-bottom flask (150 ml. capacity) fitted with a reflux condenser carrying a calcium chloride guard tube, and a thermometer. Iodine (1.98 g., 0.0078 mole) was gradually added to 3-carene. An exothermic reaction ensued. No detectable quantity of hydrogen iodide was formed. The reaction mixture had a wine-red colour. It was then heated at 174-175°C in an oil bath for 5 hours. The refluxing was smooth. A product with strong cymene odour was obtained. Qualitative test on this product with starch solution revealed the presence of iodine. Hence, the product was agitated with a 30% solution of sodium thiosulphate till free of iodine, and this was followed by a steam distillation. The steam volatile portion after drying amounted to 93.50% on the wt. of 3-carene, and had a pale yellow colour and $n_\text{D}^{30} = 1.4750$, $d_\text{D}^{30} = 0.8730$. This oil on keeping overnight developed a wine-red colour, and showed the presence of iodine (starch test). Hence, it was subjected to a three-fold distillation, each distillation taking about one hour. A deep, brown product containing free iodine (starch test) was obtained (yield 90.30%, on the wt. of 3-carene), and it was agitated with a 30% solution of sodium thiosulphate to remove the iodine, then with water, and
dried. The dried product was distilled, and the fraction boiling between 170 to 180° was collected (64% by vol.). This cut was shaken with twice its volume of 90% sulphuric acid for six hours, and the unaffected oil separated, washed with water, then with 10% sodium hydroxide solution, and finally steam distilled. The yield of the steam volatile portion after drying amounted to 20.02% on the wt. of 3-carene.

The steam volatile portion had a pale yellow colour and strong cymene odour. It had the following physical constants:  
\[ n^2_\text{D} = 1.4884, \quad d^3_\text{D} = 0.8563 \quad \text{b.p.} 170-180°/760 \text{ mm.} \]  
(78% distilling between 173-178°). Further it was free from monolefins and dielefins (Cf.p.31).

Next, the saturated oil was oxidised as fellows: A known weight of the oil (0.5234g.) was boiled three hours with a solution containing 5.2g. of potassium dichromate, 16 ml.water, 11.6 ml. sulphuric acid and 23.5 ml. acetic acid (Cf.p.94), The oxidation mixture was worked up as previously described (Cf.p.31). The yield of terephthalic acid amounted to 342.4 mg. and of isophthalic acid, 36.2 mg.

Experiment II:- This was performed in order to examine the products formed in the initial stages of the reaction between 3-carene and iodine before the refluxing procedure leading to the cymenes.
3-Carene (21.47 g., 0.1578 mole) was taken in a 150 ml.
round-bottom flask fitted with a reflux condenser connected to a
sodium chloride guard tube. Iodine (1.98 g., 0.0078 mole) was
slowly added to 3-carene. After the exothermic reaction had sub-
sided, the reaction mixture was allowed to cool, and the following
tests were performed on it.

(a) A portion of the reaction mixture was tested for
iodine in aqueous and alcoholic medium using starch solution.
There was no blue colouration, showing the absence of free iodine
in the product.

(b) The reaction mixture (0.5 ml.) was oxidised by boiling
three hours with a solution composed of 3.5g. of chromic anhydride,
15 ml. water, 5 ml. sulphuric acid and 15 ml. acetic acid. The
reaction product was worked up as previously described. It was not
possible to recover either terephthalic acid or isophthalic acid,
indicating the non-formation of p- and m-cymenes at this stage of
the reaction.

The remaining reaction mixture was kept for a week without
any protection from sunlight, and then the following tests were
performed on the oil.

(c) Starch solution was added to a portion of the reaction
mixture. There was the blue colour characteristic of iodine.
(d) The reaction mixture (0.5 ml.) was oxidised as described in test (b). Neither terephthalic nor isophthalic acid could be obtained. This showed that aromatisation into p- and m-cymenes had not occurred, and

(e) To a portion of the reaction mixture was added Beckmann's chromic acid mixture. Brown resinous flakes, characteristic of α-terpinene were formed immediately (Cf. p. 23).

Discussion:--

Till date iodine catalysed aromatisations of terpenoids have yielded only p-cymene (Cf. pp. 68, 69 and 79). Evidence is now presented to show that the aromatisation of 3-carene with iodine furnished both p- and m-cymenes.

The unaffected oil obtained by treating the fraction (b.p. 170-180°) of experiment (1) with 80% sulphuric acid was shown to be fully saturated by its failure to answer tests for monoolefins and diolefins. This clearly indicated that 80% sulphuric acid treatment was sufficient to destroy the unsaturates present in the fraction.

Further, the physical characteristics of the saturated oil compared favourably with those of p- and m-cymenes (Cf. p. 91). Confirmation as to the presence of these aromatics in the saturated oil was afforded by its oxidation to terephthalic and isophthalic acids. Based on the amounts of terephthalic and isophthalic acids
obtained, it was found that the saturated oil contained theoretically 52.79% \( \text{p-\text{cymene}} \) and 5.82% \( \text{m-\text{cymene}} \) respectively. The re-investigation of Linstead's method of estimating \( \text{p-\text{cymene}} \) showed that 450 mg. of pure \( \text{p-\text{cymene}} \) under similar conditions of oxidation should yield 474-475 mg. of terephthalic acid \((\text{Cf. p. 95})\), and based on this value, the amount of terephthalic acid obtained in the present investigation would correspond to about 61.4% \( \text{p-\text{cymene}} \). Thus a minimum of 67-68% of the saturated oil was accounted for as \( \text{p-} \) and \( \text{m-\text{cymenes}} \).

The formation of \( \text{p-} \) and \( \text{m-\text{cymenes}} \) from \( \text{3-carene} \) proved conclusively that during aromatisation, the terpene had suffered two-directional fission of its cyclopropene ring, namely at the \( \text{C}_6-\text{C}_7 \) and \( \text{C}_1-\text{C}_7 \) bonds, and from the amounts of \( \text{cymenes} \) obtained, it would seem that the fission of the \( \text{C}_6-\text{C}_7 \) bond was the more favoured mode of opening of the cyclopropane ring.

**Reaction mechanism:** In formulating a reaction mechanism for the iodine catalysed aromatisation of \( \text{3-carene} \), the following experimental observations must be accounted for: (i) the initial interaction of iodine with \( \text{3-carene} \) was attended with evolution of heat and (ii) there was no free iodine in the reaction mixture at this stage \((\text{Cf. Experiment II (b)})\).

* A corresponding value of the amount of isophthalic acid derivable from \( \text{m-\text{cymene}} \) could not be obtained due to the non-availability of pure \( \text{m-\text{cymene}} \).
Now, iodine is known to cause fission of cyclopropane (A) to yield 1,3-diiodopropane (B) and this reaction is exothermic:

\[
\text{CH}_2\text{CH} = \text{CH}_2 + \text{I}_2 \rightarrow \text{I-CH}_2-\text{CH}_2-\text{CH}_2-\text{I} \]

\(\Delta H = -17,200\) calories per mole.

A similar type of addition of iodine can be anticipated for 3-carene (VI), assuming that the ethylic linkage remains unaffected during iodination. Since the cyclopropane ring in the terpene is capable of undergoing fission in two directions i.e., at the C\(_6\)-C\(_7\) and C\(_4\)-C\(_7\) linkages, the addition of iodine would lead to the formation of diido-compounds (XXIX) and (XXX):

\[
\text{VI} \xrightarrow{[\text{I}_2]} \text{XXIX} \text{XXX} 
\]

This reaction, in analogy to the formation of diido-propane, ought to be exothermic in character. Further, it accounts for the disappearance of iodine immediately after the interaction of iodine with 3-carene.

The formation of iodine on keeping the reaction mixture (Experiment II (e)) showed that the diiodo-compounds formed were unstable, and seemed to have undergone partial decomposition, much in the same way as diiodo-propane (B) decomposing into propylene (C) and iodine:

\[
\begin{align*}
I-\text{CH}_2-\text{CH}_2-\text{CH}_2-I & \quad \longrightarrow \quad \text{CH}_3-\text{CH}=\text{CH}_2 + \text{I}_2 \\
(\text{B}) & \quad (\text{C})
\end{align*}
\]

Hence, the liberation of iodine from the postulated diiodo-compounds (XXIX) and (XXX) ought to be accompanied by the formation of \(p\)- and \(m\)-menthadienes, of which only the presence of \(\alpha\)-terpinene (IV) has been confirmed qualitatively by the action of Beckmann's chromic acid mixture (Cf. p. 100):

\[
\begin{align*}
\begin{array}{c}
\text{XXIX} \\
\text{I}
\end{array} & \quad \longrightarrow \quad \\
\begin{array}{c}
\text{IV} \\
+ \text{I}_2
\end{array}
\end{align*}
\]

The conversion of the diiodo-compounds (XXIX) and (XXX) i.e. (D) into menthadienes (E) may be represented by the general equation:

\[
\begin{align*}
\text{C}_{10}\text{H}_{16}\text{I}_2 & \quad \longrightarrow \quad \text{C}_{10}\text{H}_{16} + \text{I}_2 \\
(\text{D}) & \quad (\text{E})
\end{align*}
\]

1. Freund, Montash, 1881, 2, 640.
Further, no cyrenes could be detected in the reaction mixture before its refluxing and distillation (Experiment II (b) and (d)). Evidently then, these two operations seem to have caused the accelerated decomposition of the diiodo-compounds, and also the aromatisation into the cyrenes.

Now it may be recalled, that Ipatieff and co-workers (Cf. pp. 69 and 79) have found that monocyclic olefinic compounds (F) containing two double bonds per molecule undergo hydrogen transfer on distillation with catalytic amounts of iodine to yield aromatic (G) and cyclic monoolefinic (H) counterparts:

\[
2 \text{C}_{10}\text{H}_{16} \rightarrow \text{C}_{10}\text{H}_{14} + \text{C}_{10}\text{H}_{18}
\]

(F) \hspace{2cm} (G) \hspace{2cm} (H)

(e.g. terpinene and limonene into \(p\)-cyrene).

Although the cyclic monoolefinic products have not been identified in the present investigation, the formation of \(p\)- and \(m\)-cyrenes on refluxing and distilling the reaction mixture may best be ascribed to a similar type of iodine catalysed disproportionation of \(p\)- and \(m\)-menthadienes respectively, which are formed by the decomposition of the diiodo-compounds (XXIX) and (XXX), the iodine required for the transformation being furnished by the decomposition of these compounds.
Summary.

(1) 3-Carene has been aromatised into p- and m-symenes under the catalytic influence of iodine. This is a new observation. So far, no terpeneid has yielded the two aromatics simultaneously on iodine aromatisation.

(2) The fact that both p- and m-symenes result by the aromatisation with iodine shows that the two-directional fission of the cyclopropane ring of 3-carene had taken place at the C₆-C₇ and C₁-C₇ linkages.

(3) From the amounts of p- and m-symenes estimated on the basis of the terephthalic and isophthalic acids respectively, it appears that the fission of the C₆-C₇ linkage is the more favoured route of opening the cyclopropane ring of 3-carene.

(4) The aromatisation of 3-carene into p- and m-symenes establishes the structural relationship of the terpene to these aromatics.

(5) A mechanism has been suggested to account for the aromatisation observed.
(II) Aromatisation of 3-carene with Bromine:

Experiment III:— 3-Carene (21.25 g., 0.1562 mole) was taken in a 150 ml, round-bottom flask and chilled in freezing mixture (ice-salt). Bromine (24.96 g., 0.1562 mole) cooled in freezing mixture was added to 3-carene drop-wise with occasional agitation. The addition of bromine was attended with very slight formation of hydrogen bromide. The reaction mixture was brownish-red in colour. It was next refluxed for 21 hours over a naked flame. There was copious evolution of hydrogen bromide. The fuming reaction mixture was cooled, then neutralised with 10% sodium hydroxide solution and finally steam distilled. The steam volatile portion after drying amounted to 72.2% on the weight of 3-carene, and had $\mu^{20}_D$ 1.4901. The 170 to 180° fraction of this liquid (65% by vol.) was shaken with twice its volume of 80% sulphuric acid for 6 hours to destroy the unsaturates present. The unaffected portion was separated, washed repeatedly with water, then successively with 10% sodium hydroxide and water, and finally steam distilled. The steam distillate after drying amounted to 48.18% (on the wt. of 3-carene), and had $\mu^{20}_D$ 1.4917. Careful fractionation of this steam distillate gave a pale yellow saturated oil, free from bromine (qualitative test), and with strong eymene odour (yield: 26.3% on the wt. of 3-carene). The saturated oil had the following physical constants: b.p.170-180° / 760 mm. (75% boiling between 174-178°), $\mu^{20}_D$ 1.4986, $d^{31}_2$ 0.8592.
Oxidation of 0.4823 g. of the saturated oil by boiling with a mixture of 4.8134 g. of potassium dichromate, 10.7 ml. sulphuric acid, 21.4 ml. acetic acid and 16 ml. water for 3 hours, gave 283.9 mg. of terephthalic acid and 89 mg. of isophthalic acid.

Discussion:
The bromine-free saturated oil in this investigation had physical constants akin to those of p- and m-cymenes (Cf. p. 91). Conclusive evidence of the presence of these hydrocarbons in the saturated oil was furnished by oxidation to terephthalic and isophthalic acids. The yields of the terephthalic and isophthalic acids were theoretically equivalent to 48.38% p-cymene and 14.54% m-cymene respectively. Based on the value that 450 mg. of pure p-cymene would yield under similar conditions of oxidation 475 mg. of terephthalic acid, the yield of p-cymene in the present investigation would amount to 55.72%. Thus at least 70.26% of the saturated can be accounted as cymenes. Further, these results clearly show that the cyclopropane ring of 3-carene had undergone fission at the C₆-C₇ and C₄-C₇ linkages and preferentially at the former linkage.

Up to the present, no terpenoid has furnished p- and m-cymenes simultaneously by bromine dehydrogenation. The terpenoid that gave only m-cymene using the bromine dehydrogenation technique is sylvestrene, and this was accomplished by the Baeyer-Villiger method (Cf. p. 85).
Thus the simultaneous formation of p- and m-cymenes in the present investigation is a new type of transformation in terpene chemistry. Further, the conversion establishes the structural relationship of 3-carene to these aromatics.

In contradistinction to the observations of Baeyer and Villiger, Olsen found that for dehydrogenation with bromine, it is the incomplete bromination that offers a guarantee to aromatisation by the thermal method (Cf. pp.72-74). In agreement with this, the present investigation has shown that the aromatisation of 3-carene into p- and m-cymenes can be effected by using molar proportion of bromine, and that there is no need to resort to Baeyer-Villiger method.

Reaction mechanism:— It has been reported\(^1\) earlier that with bromine in chloroform solution, 3-carene reacts readily, one mole of bromine being absorbed, but the dibromide is unstable and evolved hydrogen bromide.

Now the addition of bromine to 3-carene in molar proportions as described in the experiment was a smooth process, attended with very little evolution of hydrogen bromide. The mode of fixation of the bromine atoms to 3-carene can take place

---
in two possible ways: (i) bromine saturates the double bond in 3-carene (VI) to yield the dibromide (XXXI), assumption being made that the cyclepropane ring remains intact during bromination, and (ii) bromine causes the cleavage of the cyclepropane ring two-directionally at the C₆-C₇ and C₇-C₈ linkages, to yield respectively the dibromides (XXXII) and (XXXIII):

While the first possibility is in conformity with the normal addition of halogens to the ethenoid linkage, the second possibility is justified because it is known that bromine can rupture cyclepropenes, as for instance in the conversion of cyclepropane into 1,3-dibromopropane.

On refluxing, the dibromide-compound (XXXI) gives off hydrogen bromide, as has been indicated in the experimental section, and as is known from the observation made by Simensen,

and suffer at the same time a two-directional rupture of the
cyclopropane ring to give p- and m-cymenes, (I) and (XXXIV). The
dibromides (XXXII) and (XXXIII) can yield p-cymene (I) and m-cymene
(XXXIV) respectively by elimination of two molecules of hydrogen
bromide. These reactions are represented in the following
equations:

\[
\begin{align*}
&\text{XXXI} \\
&\begin{array}{c}
\begin{array}{c}
\text{XXXII} \\
\text{XXXIII}
\end{array}
\end{array} \\
&\begin{array}{c}
\begin{array}{c}
\text{XXXIV}
\end{array}
\end{array}
\end{align*}
\]
Summary.

(1) The conversion of 3-carene into p- and m-cyrenes with bromine is rather novel in terpene chemistry. Further it establishes the structural relationship of 3-carene to both p- and m-cyrenes.

(2) The aromatisation of 3-carene into the cyrenes by using bromine equivalent to two atoms, fully confirms Olsen's idea that it is the incomplete bromination that offers a guarantee to successful aromatisation by the bromine dehydrogenation technique.

(3) The simultaneous formation of p- and m-cyrenes from 3-carene shows that the cycloprene ring of the latter has opened up two-directionally by rupture of the C₆-C₇ and C₇-C₈ bonds. From the amounts of cyrenes, it appears that the fission of the C₆-C₇ bond is the more favoured mode of decyclising 3-carene.

(4) A mechanism has been suggested to account for the aromatisation of 3-carene with bromine.
A mixture of 3-carene (136 g., 1 mole), sulphur (40 g., 1.25 moles) anhydrous zinc chloride (2 g.) and active carbon (2 g.) (Scherer-Kahlbaum) were heated together at 159-161° in an oil bath for 8 hours in a 3-necked flask fitted with a reflux condenser carrying a calcium chloride guard tube, thermometer and stirring equipment. At the end of the period of refluxing, there was still the evolution of hydrogen sulphide. Steam distillation of the deep brown viscous reaction mixture, gave a pale yellow coloured liquid, which after drying amounted to 43.83% on the weight of 3-carene and it had $\alpha_{D}^{30}$ 1.4801, $d_{D}^{30}$ 0.8640. The unsaturates in the steam volatile oil were destroyed by shaking with twice its volume of 80% sulphuric acid for 6 hours. The unaffected oil was separated, washed repeatedly with water, then with 10% sodium hydroxide, again with water, and finally steam distilled. The steam distillate after drying amounted to 7.30% on the weight of 3-carene, and it had the following physical characteristics: $\alpha_{D}^{30}$ 1.4868, $d_{D}^{30}$ 0.8630, b.p. 173-180°/760 mm. (80% distilling between 174.5 to 177.5°), pale yellow colour and strong eymene odour. A portion of this steam distillate was shaken with concentrated sulphuric acid and it was found unaffected, showing thereby the absence of unsaturates in it.

Further, it was tested qualitatively for sulphur, with negative result. Oxidation of 431 mg. of this oil by refluxing 3 hours with a mixture of chromic anhydride (3.5g.) sulphuric acid (5 ml) acetic acid(15 ml.) and water (15 ml.) gave 207 mg. of terephthalic acid and 109 mg. of isophthalic acid, theoretically equivalent to 38.8% p-cymene and 20.24% m-cymene respectively. Based on the value that 450 mg. of pure p-cymene under similar conditions of oxidation would yield 424 mg. of terephthalic acid (Cf.p.94), the yield of p-cymene in the saturated oil would amount to 50.97%.

Experiment V: Aromatisation with Sulphur:

3-Carene (34 g., 0.2300 mole) and sulphur (9.4 g., 0.2941 mole) were refluxed together at 170-205° in an oil bath for 40 hours in a 2-necked flask (150 ml. capacity) fitted with a reflux condenser carrying a calcium chloride guard tube and a thermometer. At the end of the period of refluxing, there was still the evolution of hydrogen sulfide, steam distillation of the deep brown viscous reaction mixture yielded an oil from which the fraction boiling at 170-185° was cut, amounting to 18.58% on the weight of 3-carene. Qualitative test on this fraction for α-terpinene with Baekmann's chromic acid mixture was positive,

whilst Wallash's test with $\text{Ag}_2\text{O-H}_2\text{SO}_4$ gave only a purple colouration (Cf. p. 23). The unsaturates in this fraction were destroyed by shaking it with twice its volume of 80% sulphuric acid for 9 hours; the unreacted oil was separated, repeatedly washed with water, then with 10% sodium hydroxide solution, and finally steam distilled; yield after drying amounted to 13.61% on the weight of 3-carene, with $\delta^29_D$ 1.4955, $\delta^{31}_D$ 0.8507, b.p. 174–176°C/760 mm. The oil had a pale yellow colour and strong cymene odour. On shaking a portion of the oil with concentrated sulphuric acid, it remained unaffected, thus indicating its saturated character. Oxidation of 0.4486 g. of the oil by refluxing 4 hours with a mixture of 4.4590 g. potassium dichromate, 10 ml. concentrated sulphuric acid, 20 ml. acetic acid and 15 ml. water furnished terephthalic acid (yield 192.2 mg.) and isophthalic acid (yield 148.8 mg.) theoretically equivalent to 34.57% p-cymene and 26.77% m-cymene respectively. Based on the value that 450 mg. of pure p-cymene on oxidation would yield 475 mg. of terephthalic acid, the yield of terephthalic acid obtained in the present investigation would correspond to 40.58% p-cymene.

**Discussion:**

Experiment IV, conducted essentially on the lines suggested by Guha et al. (except perhaps in the nature of the active charcoal) confirmed the ability of sulphur in conjunction with active
carbon and zinc chloride to aromatise 3-carene into p-cymene as has been reported by the earlier investigators, but also to m-cymene. The conversion of 3-carene into p- and m-cymenes is in conformity with the theoretical possibility that the cyclopropane ring of the terpene can undergo two-directional rupture at the C6-C7 and C4-C7 linkages. From the theoretical amounts of p- and m-cymenes calculated on the basis of terephthalic and isophthalic acids respectively (38.8% p- and 20.24% m-), it would appear that the fission of the C6-C7 bond was the more favoured mode of opening up of the cyclopropane ring in 3-carene. Further, the two-way aromatisation of 3-carene established the structural relationship of 3-carene to both p- and m-cymenes.

It is significant that this is the first instance where a terpenoid yielded p- and m-cymenes simultaneously by sulphur aromatisation.

Experiment V was performed with a view to find out whether sulphur alone can bring about the aromatisation of 3-carene into p- and m-cymenes. The results obtained clearly demonstrated that this was possible. The yield of saturated oil amounted to 13.61% as against 7.30% of experiment IV. This shows that the use of the auxiliary agents, carbon and zinc chloride, had no appreciable beneficial effects on the aromatisation; instead they
seemed to cause the loss of 3-carene either as sulphurised or polymerised products, the nature of which was not further investigated. Moreover, the theoretical amounts of p- and m-cymenes in the saturated oil amounted to 34.57% and 26.77% respectively, i.e., a total of 61.34% cymenes as against 59.04% in experiment IV. Evidently then, sulphur alone can fulfil the two-directional aromatisation of 3-carene in a more efficient manner than sulphur in conjunction with active carbon and zinc chloride.

An interesting feature in experiment V was the presence of α-terpinene in the steam volatile portion of the reaction mixture. The formation of this p-menthaediene suggested that sulphur can also function as an isomerising agent. Whether this was achieved by a direct mechanism or by attack of proton derived by the ionisation of hydrogen sulphide \( \text{H}_2\text{S} \rightarrow \text{H}^+ + \text{HS}^- \) is not certain (Cf.p.55). No attempt was however made to find out the nature of the other possible p-isomers that might have arisen during the reaction. Although no \( \text{m} \)-isomers could be detected by the \( \text{Ag}_2\text{O}-\text{H}_2\text{SO}_4 \) test, the possibility of their intermediate formation by the fission of the \( \text{C}_1-\text{C}_7 \) linkage is not excluded in order to explain the formation of \( \text{m} \)-cymene.

**Reaction mechanisms:** Two possible mechanisms may be suggested to account for the aromatisation of 3-carene into \( \text{p} \)- and \( \text{m} \)-cymenes, namely, (1) Addition mechanism and (2) Free radical mechanism.
(1) Addition mechanism: In this mechanism, the aromatisation of 3-carene (VI) into p- and m-cymenes (I) and (XXXIV), is believed to take place via the sulphurised product (XXXV) formed by the addition of sulphur to the double bond of 3-carene, assuming that the cyclopropane ring of the latter remains in tact during the addition of sulphur. The formation of ethylene sulfide rings is not uncommon by the interaction of sulphur with terpenoids. In view of the known instability of these rings, decomposition of (XXXV) takes place with elimination of hydrogen sulphide and two-directional opening of the cyclopropane ring giving rise to p- and m-cymenes.

As has been mentioned, the isomerisation of 3-carene might have preceded aromatisation. The aromatisation of p- and m-isomers formed may be visualised as involving the formation of

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1. Cf.p.76.
2. Nakatsuchi, refs.8 and 14), p.75.
sulphurised products by one to one addition of sulphur across a double bond, followed by elimination of hydrogen sulphide to give rise to the aromatics. Thus, the aromatisation of α-terpinene (IV) to p-cymene (I) may be represented by the following equations:

\[ \text{IV} \xrightarrow{S} \text{XXXVI} \xrightarrow{\text{-H}_2\text{S}} \text{I} \]

(2) Free radical mechanism:— The reactions of olefins and poly-olefins with sulphur have been discussed by Farmer and Shipley\(^1\). These investigators suggest that sulphur acts in these reactions by a free radical mechanism involving either the unsaturation electrons of the hydrocarbons or the active methylene groups.

In the reaction under consideration, the sulphur atom or a molecular chain, \((\text{S}_n)\), where \(n = 2 \text{ to } 8\) is believed to act as a radical in the dehydrogenation steps\(^2\). This is because, in

the liquid sulphur, the equilibrium \( S_g \rightleftharpoons S_n \) (chain) prevails\(^1\).

At the temperature near the melting point, the \( S_g \) molecules predominate, and as the temperature rises to 160\(^\circ\)C, these molecules get ruptured. Thus for instance, the symmetrical splitting of the \( S_g \) ring (XXXVIII) would furnish the radical \( \cdot(S_g) \). (XXXIX) as represented below:

The attack by sulphur may begin by displacement of \( \alpha \)-methylene hydrogen atoms\(^2\) of 3-carene (VI) at the 2 and 5 positions to yield the free radicals (XL) and (XLI):

The HS radicals formed, being effective hydrogen acceptors, take part in subsequent reaction steps.\(^1\)

The radicals (XL) and (XII) can achieve stabilisation in two ways: (a) by donating a second hydrogen from the reactive unattacked \(-\text{CH}_2-\) group to the HS radicals, with opening of the cyclopropane ring two-directionally by fission of the C\(_6\)-C\(_7\) and C\(_1\)-C\(_7\) linkages, giving rise to p- and m-cymenes respectively with evolution of hydrogen sulphide:

and (b) by disproportionation\(^2\) thus: \(2 \text{C}_10\text{H}_{15}. \rightarrow \text{C}_10\text{H}_{14} + \text{C}_10\text{H}_{16}.\)

leading to the cymenes and menthadienes, of which \(\alpha\)-terpinene has been detected.

It may be pointed out that in this mechanism the attack by sulphur on \(\alpha\)-methylenes predominates over addition at the double bond.

Summary.

(1) Under the influence of sulphur, the cyclopropane ring of 3-carene suffers decyclisation two-directionally to give \( \pi \) and \( \mu \)-cymenes. Thus for the first time, a terpene has been aromatised simultaneously into \( \pi \)- and \( \mu \)-cymenes using sulphur.

(2) The sulphur aromatisation of Guha et al has been repeated, and it is clearly demonstrated that their observation that only \( \pi \)-cymene is obtained from 3-carene with sulphur in conjunction with active carbon and zinc chloride must be regarded as incomplete in view of the above remarks.

(3) The formation of \( \pi \) and \( \mu \)-cymenes establishes the structural relationship of 3-carene to these aromatics.

(4) Sulphur, apart from acting as a dehydrogenating agent giving the cymenes, seems also to induce isomerisation of 3-carene, e.g. into \( \alpha \)-terpinene.

(5) Two mechanisms have been proposed to account the aromatisation of 3-carene into \( \pi \) and \( \mu \)-cymenes and intermediate formation of \( \alpha \)-terpinene.
(IV) Aromatisation of 3-carene with Chloracetic acids:

Experiment VI:-- Aromatisation with trichloracetic acid:

3-Carene (51.02 g., 0.3750 mole) and trichloracetic acid
(3.32 g., 0.05087 mole) were refluxed together at 170-180° for
10 hours, precaution being taken to exclude moisture. Steam distil­
lation of the light, orange coloured, viscous reaction mixture
after neutralisation with 10% sodium hydroxide solution, yielded
a pale yellow oil, which after drying amounted to 20.42% on the
weight of 3-carene, and had the following physical constants:
\[ n_D^{20} 1.4805, \text{ b. p. } 170-184^\circ/760 \text{ mm.} \] On treatment
with Beckmann's chromic acid mixture, the oil gave immediately
brown resinous flakes, indicating the presence of \(\alpha\)-terpinene
(Cf.p.23), and in acetic anhydride with a drop of concentrated
sulphuric acid, it gave a transient violet colouration, probably
indicating the presence of m-menthadienes\(^1\). The 170-184° cut was
shaken with twice its volume of 90% sulphuric acid for 6 hours to
destroy the unsaturates present in it, and the unreacted oil was
separated. It was successively washed with water, 10% sodium
hydroxide solution, and finally steam distilled. The steam distil­
late after drying amounted to 13.85% on the weight of 3-carene, and
had \[ n_D^{20} 1.4890, \text{ b. p. } 170-180^\circ/760 \text{ mm.} (80\% \text{ by vol. boiling at}
174-175^\circ) \]. It was pale yellow in colour and had strong odour of
cymene. Qualitative test showed that it was free from chlorine.

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On shaking a portion of the oil with concentrated sulphuric acid, it remained unaffected, thus indicating its saturated character.

Oxidation of 0.4376 g. of the oil by refluxing 3 hours with a mixture composed of potassium dichromate (4.92 g.), water (17 ml.), sulphuric acid (11 ml.) and acetic acid (22 ml.) gave 192.4 mg. of terephthalic acid and 85.8 mg. of isophthalic acid, theoretically equivalent to 31.85% p-cymene and 14.20% m-cymene. Based on the fact that 450 mg. of pure p-cymene under similar conditions of oxidation would yield 475 mg. of terephthalic acid, the yield of terephthalic acid obtained in the above oxidation would correspond to 37.47% p-cymene.

**Experiment VII: Aromatisation with monochloracetic acid:**

3-Carene (51.02 g., 0.3750 mole) and monochloracetic acid (4.743 g., 0.05087 mole) were refluxed together for 10 hours at 170-180°, precaution being taken to exclude moisture. The reaction mixture obtained was light yellow in colour and slightly viscous. It was neutralised with 10% sodium hydroxide solution and then steam distilled. The steam distillate after drying amounted to 75.75% on the weight of 3-carene and had the following physical characteristics: pale yellow colour, lemon odour, n^20_D 1.4737, 67.9% (by vol.) boiling at 170-184°/760 mm. The 170-184° cut gave positive indication of α-terpinene with Beckmann's chromic acid mixture, but it showed no characteristic colouration.
with \( \text{Ac}_2\text{O}-\text{H}_2\text{SO}_4 \) (Cf. p.23). This oil was next treated with 80% sulphuric acid on the lines suggested in the above experiment, and the saturated oil after drying amounted to 4.96% on the weight of 3-carene. It was free from chlorine (qualitative test), and fully saturated in character (concentrated sulphuric acid test). The saturated oil had pale yellow colour and cymene odour and n\(^D\) 1.4870, b.p. 173-178\(^\circ\)/760 mm. Oxidation of the saturated oil (0.2629 g.) by refluxing 3 hours with a mixture of potassium dichromate (3.1021 g.), water (10.4 ml.), acetic acid (14 ml.) and sulphuric acid (7 ml.) gave 61.6 mg. terephthalic acid and 46.2 mg. isophthalic acid, theoretically equivalent to 18.91% p-cymene and 14.18% m-cymene respectively. Based on the value that 450 mg. of pure p-cymene would yield 475 mg. of terephthalic acid, the percentage of p-cymene in the saturated oil would amount to 22.2.

**Discussion:**

Ipatieff and his co-workers\(^1\) introduced chloracetic acids as aromatising catalysts in terpene chemistry. They found that monocyclic terpenes having rings with 6 carbon atoms and 2 double bonds per molecule (e.g. limonene, terpinene), on refluxing with chloracetic acids, underwent disproportionation according to the equation 
\[
2 \text{C}_{10}\text{H}_{16} \rightarrow \text{C}_{10}\text{H}_{14} + \text{C}_{10}\text{H}_{18},
\]
giving rise to p-cymene and monoolefinic counterparts, the activity of the catalysts being

\(^1\) Ipatieff, Pines and Olberg, ref.(1), p.69.
of the order: trichloracetic acid > dichloracetic acid > monochloracetic acid.

In the present investigations the formation of p- and m-cymenes may be explained by a mechanism similar to that suggested earlier (Cf. pp. 58-60).

A comparison of the results obtained with trichlor- and monochlor- acetic acids leads to some interesting conclusions. The saturated oil using trichlor- and monochlor- acetic acids amounted to 13.85% and 4.96%, with theoretically 31.85% and 18.91% p-cymene, 14.20% and 14.18% m-cymene respectively. From this it follows that (i) trichloracetic acid is a superior aromatising catalyst than monochloracetic acid (ii) in both cases, the amount of p-cymene formed is in greater proportion than of m-cymene and (iii) from the amount of p-cymene formed, the fission of the C₆-C₇ linkage seems to be the more favoured mode of opening of the cyclopropane ring of 3-carene.

Although trichloracetic acid gives better yields of the aromatics, a serious drawback of this catalyst is that it destroys about 90% of 3-carene as non-steam volatile products, as against about 25% in the case of monochloracetic acid. The non-steam volatile portions are presumed to be mainly chloroacetates.

Lastly, the aromatisation of 3-carene to give p- and m-cymenes simultaneously using chloracetic acids is a new finding in terpene chemistry.
Summary.

(1) 3-Carene has been aromatised into p- and m-cymenes by the action of trichlor- and monochlor- acetic acids. p-Cymene is formed in greater amounts than m-cymene. This is a new finding in terpene chemistry.

(2) Trichloracetic acid is a superior aromatising catalyst than monochloracetic acid.

(3) The aromatisation has been explained on the basis of carbonium ion theory.

(V) Aromatisation of 3-carene with Phosphorus pentoxide:

Experiment VIII:—Phosphorus pentoxide (about 2.7 g.) was quickly transferred into a round-bottom flask (150 ml. capacity) containing 3-carene (25.51 g., 0.1875 mole), fitted with a reflux condenser and a calcium chloride guard tube, and refluxed for 10 hours at 170-180°. A light brown fluorescent oil was obtained which had the odour of cymene. Steam distillation of the reaction mixture gave a clear oil, which after drying amounted to 47.64% on the weight of 3-carene, and had $\n_{D}^{30} 1.4700$, $d_{50}^{30} 0.9271$. The steam distillate yielded a cut amounting to 31.0% on the weight of
3-carene, with a boiling range 170-180°/760 mm. Interaction of Beckmann's chromic acid mixture with a portion of this product gave immediately brown resinous flakes indicating the presence of α-terpinene (Cf.p.23). The unsaturates in the 170-180° fraction were destroyed by shaking 6 hours with twice its volume of 90% sulphuric acid, and the unaffected oil amounted to 23.0% on the weight of 3-carene, and had n\textsubscript{D}^{30} 1.4855, d\textsubscript{30}^{30} 0.8532, b.p.173-178°/760 mm., pale yellow colour and cymene odour. A portion of the oil on treatment with concentrated sulphuric acid remained unaffected showing thereby that it was fully saturated in character. Oxidation of 0.4539 g. of the saturated oil with potassium dichromate gave 221 mg. of terephthalic acid and 84 mg. of isophthalic acid, theoretically equivalent to 37.96% p-cymene and 14.43% m-cymene. Based on the fact that 450 mg. of pure p-cymene on oxidation would yield 475 mg. of terephthalic acid, the yield of terephthalic acid obtained in the above oxidation would correspond to 46.61%.

Discussion:

In terpene chemistry, phosphorus pentoxide has been used for the aromatisation of camphor to p-cymene (Cf.p.82) and fenchene to m-cymene (Cf.pp.85,86), and also as an auxiliary agent in the
sulphur aromatisation of camphene to p-cymene. Now it has been shown that phosphorus pentoxide can cause the aromatisation of 3-carene to yield p- and m-cymenes simultaneously.

This is a new observation in terpene chemistry, namely a terpene hydrocarbon yielding p- and m-cymenes simultaneously on interaction with phosphorus pentoxide.

A probable mechanism for the aromatisation of 3-carene into the cymenes is the following: If it is assumed that traces of water can act as co-catalyst, then, the fission of the cyclopropane ring of 3-carene by acceptance of proton from phosphoric acid formed by the dissolution of phosphorus pentoxide in traces of water, results in carbenium ions (XXX) and (XXXI) represented on page 55, which would explain the formation of p- and m-cymenes along the same lines as given earlier (Cf. pp. 58-60).

From the theoretical amounts of p- and m-cymenes evaluated on the basis of terephthalic and isophthalic acids respectively, it is seen that the yield of p-cymene is greater than that of m-cymene (approximately in the ratio 3:1), and consequently, the fission of the C₆-C₇ linkage seems to be the more favoured route of opening the cyclopropane ring of 3-carene.

Summary.

(1) For the first time, a terpene hydrocarbon has been aromatised into p- and m-cymenes simultaneously by interaction with phosphorus pentoxide.

(2) p-Cymene is obtained in greater yield than m-cymene.

(3) The aromatisation may be explained on the basis of carbenium ion theory.
PART VI—SUMMARY OF SECTION C:

(1) The production of \( p- \) and \( m- \)cylenes from various sources, and also of the purification, identification and estimation of these aromatics have been reviewed in outline.

(2) Linstead's semi-quantitative method of estimating \( p- \)cyrene by oxidation into terephthalic acid has been re-investigated and necessary modifications have been suggested.

(3) Aromatisation of 3-carene using iodine, bremine, sulphur in conjunction with zinc chloride and active carbon, sulphur, trichloracetic acid, mesoehloracetic acid and phosphorus pentoxide has been investigated. The significant features of these liquid phase aromatisations may be briefly stated as follows:

(a) The cyclopropane ring of 3-carene opens up in all cases by fission of the \( C_6-C_7 \) and \( C_7-C_8 \) linkages, furnishing \( p- \) and \( m- \)cylenes respectively. The yields of the cylenes obtained in these aromatisations are summarised in Table V on page 130.

(b) As can be seen from Table V, the efficiency of the aromatising agents is in the order: bremine > phosphorus pentoxide > iodine > sulphur > trichloracetic acid > sulphur + zinc chloride + active carbon > mesoehloracetic acid.
The weight of 5-cisene.

**Theoretical** based on the terephthalic acid isolated.

Theoretic based on the isophthalic acid isolated.

Based on the value of terephthalic acid obtained by the oxidation of pure p-cymene.

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Aromatising agent.</th>
<th>Saturated oil (%)</th>
<th>p-Cymene %</th>
<th>m-Cymene %</th>
<th>p + m</th>
<th>p'-m</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>I₂</td>
<td>20.02</td>
<td>52.79</td>
<td>5.92</td>
<td>58.61</td>
<td>61.40</td>
</tr>
<tr>
<td>III</td>
<td>Br₂</td>
<td>26.30</td>
<td>48.39</td>
<td>14.54</td>
<td>62.92</td>
<td>55.72</td>
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<tr>
<td>IV</td>
<td>S + ZnCl₂ + C</td>
<td>7.30</td>
<td>39.80</td>
<td>20.24</td>
<td>59.04</td>
<td>50.97</td>
</tr>
<tr>
<td>V</td>
<td>S</td>
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<td>34.57</td>
<td>26.77</td>
<td>61.34</td>
<td>40.58</td>
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<td>CCl₃COOH</td>
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<td>31.85</td>
<td>14.20</td>
<td>46.05</td>
<td>37.47</td>
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<tr>
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<td>CH₂CICOOH</td>
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<td>18.91</td>
<td>14.18</td>
<td>33.09</td>
<td>22.20</td>
</tr>
<tr>
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<td>P₂O₅</td>
<td>23.00</td>
<td>37.96</td>
<td>14.43</td>
<td>52.39</td>
<td>46.61</td>
</tr>
</tbody>
</table>

Table V:

Summary of the Aromatisation Experiments.
(c) The most striking feature of these experiments is the formation of p-cymene in greater amounts than of m-cymene. This indicates that the fission of the C₆-C₇ linkage is the more favoured route of opening of the cyclopropane ring of 3-carene.

(4) Hitherto no terpene hydrocarbon has furnished p- and m-cymenes simultaneously on aromatisation. As regards 3-carene Guha and his co-workers identified only p-cymene on aromatisation of the terpene with sulphur in presence of various promoters. Further, the aromatisation of the terpene by dehydration with dilute sulphuric acid of its α-glycol obtained by oxidation with potassium permanganate in alkaline solution, yielded only p-cymene¹. Hence, the aromatisations under consideration wherein both p- and m-cymenes have been obtained constitute a new set of transformations in terpene chemistry.

(5) Further, the aromatisation of 3-carene into p- and m-cymenes establishes for the first time, the structural relationship of the terpene to these aromatics. 3-Carene has, thus, a unique status, for, so far, no other terpene has been found to have such a dual relationship to the cymenes. Consequently, 3-carene seems to be one of the connecting links between the p- and m-series of terpenes. This relationship would appear rather anomalous on the basis of the classical concept that no terpene is

found to have structural relationship to α-cymene, let alone to
p- and m-cymenes simultaneously. Although much more experimental
work is needed, it may be tentatively suggested that terpenes of
the monocyclic and bicyclic systems may be divided into three
groups: (i) terpenes with structural relationship to p-cymene,
e.g., limonene, terpinolene, α- and β-terpinenes (ii) terpenes
with structural relationship to p- and o-cymenes, e.g., α-pinene,
β-pinene and (iii) terpenes with structural relationship to p-
and m-cymenes, e.g., carenes.

Moreover, the conversion of 3-carene into p- and
m-cymenes lends additional support to the structure assigned to
3-carene by Simonsen and his co-workers. Earlier, the presence
of the cyclohexane ring in 3-carene was based on the formation
of sylvestrene and dipentene dihydrochlorides on hydrochlorination
of the terpene. Now, the aromatisation of 3-carene into p- and
m-cymenes not only substantiates the existence of the 6-membered
carbon framework in the terpene, but also the position assigned
to the cyclopropane ring (i.e. between C₁ and C₆) by other
considerations.

Reaction mechanisms have been proposed to explain
the formation of p- and m-cymenes from 3-carene in these investi-
gations.
(9) Lastly, the conversion of 3-carene into m-cymene offers possibility of utilisation of a new raw material for the production of m-cymene. A perusal of literature does not reveal a single patent on the production of m-cymene from terpenoids. This is probably due to the absence of terpenes with m-cymene carbon framework. Now that 3-carene, which can be recovered from turpentine oils on industrial scale, has been proved to be a potential raw material for the production of m-cymene, it is hoped that these investigations would lead to further experimentation and standardisation of efficient methods for the production of m-cymene on an industrial scale.