This section comprises of the following parts:

Part I: Literature survey
Part II: Experimental
Part III: Discussion and
Part IV: Summary.

PART I- LITERATURE SURVEY:

The Swedish patent\(^1\) granted to Kungl Armeförvaltningens Artilleri department in 1938 first announced the use of pure 3-carene as a raw material for the production of p-cymene. The details disclosed in the patent refer to the aromatisation of the terpene at 350-450\(^\circ\) in contact with a catalyst consisting of finely dispersed porous mixture of silicic acid and one or more of the following metals or their oxides or sulphides: nickel, cobalt and copper.

From 1943 onwards Verghese and co-workers studied the vapour phase aromatisation of 3-carene into p-cymene, using


\(^1\) Swedish patent (inventors, Skarbloa and Linder), June 8,1938, 92,484 (Amer.Chem.Abs.1939,21, 1764).
catalysts such as partially dehydrated gypsum\textsuperscript{1}, ferric oxide impregnated on partially dehydrated gypsum\textsuperscript{2}, partially dehydrated ferrous sulphate\textsuperscript{3}, zinc oxide\textsuperscript{4} and silica\textsuperscript{5}. A significant discovery made during the course of these investigations was that partially dehydrated gypsum could function as an aromatising catalyst, and this was subsequently confirmed by Sondhi and co-workers by the aromatisation of 3-carene into p-cymene\textsuperscript{6}. The later investigators also studied the aromatisation of 3-carene using vanadium pentoxide catalyst. In all these investigations only p-cymene was reported to have been found in the cymene fraction of the catalysates.

The next advance on the study of the aromatisation of 3-carene was due to Guha, Roy and Paul\textsuperscript{7}, using chromium-aluminium oxide, and nickel formate on keiselghur and on pumice stone as

3. Verghese, Sondhi, Bhushan and Joshi, ibid, 1949,\textbf{17}, 999.
catalysts. With 10% Cr₂O₃ on alumina as catalyst, 55-60% yield of p-cymene was effected from the terpene in the neighbourhood of 500°. Similar conversion was achieved with the other catalysts also. It had been stated that the formation of p-cymene as the predominant product of catalytic reaction confirmed by oxidation of the oil to p-toluic acid indicated that m-cymene, the other probable product, underwent irreversible isomerisation; thus the catalytic reaction involved simultaneous rupture of the cyclopropane ring, migration of the isopropyl group followed by dehydrogenation.

Later, Sondhi¹ investigated the aromatisation of 3-carene with chromium-aluminium oxide catalyst. With 20% Cr₂O₃ on alumina, at about 400° and liquid hourly space velocity of 0.21, 55% conversion into p-cymene (85% purity) was achieved.

A very recent publication² of great interest was the disproportionation of 3-carene with activated carbon catalyst. At 410-430°, the terpene reacted according to the equation:

\[ 3 \text{C}_{10}\text{H}_{16} \rightarrow 2 \text{C}_{10}\text{H}_{14} + \text{C}_{10}\text{H}_{20} \]

showing that the opening of the cyclopropane ring was followed by disproportionation.

Finally, Ljuggren\(^1\) converted 3-carene into p-cymene using a nickel catalyst.

In all the aromatisations of 3-carene as far achieved, only p-cymene has been reported. Nevertheless, a consideration of the structure of 3-carene permits one to infer that the cyclopropane ring of 3-carene can theoretically open up two-directionally at the C\(_6\)-C\(_7\) and C\(_1\)-C\(_7\) linkages to yield p- and m-cymenes respectively. This assumption is further justified by the fact that in the liquid phase aromatisations reported in section C, both p- and m-cymenes have been obtained. Work done in this Laboratory has provided ample evidence for the two-directional aromatisation of 3-carene in the vapour phase, and in the following part an experiment is reported with chromium-aluminium oxide catalyst wherein this type of transformation has been realised.

PART II- EXPERIMENTAL:

3-Carene:- The 3-carene used in this investigation was separated from Indian turpentine oil of Pinus longifolia (Roxb) as described on page 19.

Chromium-aluminium oxide catalyst.

(a) Preparation of \(\kappa\)-alumina:- The \(\kappa\)-alumina was prepared through precipitation of the hydroxide by carbon dioxide

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from a solution of potassium aluminate as recommended by Bischens and Selwood.

Three moles of potassium hydroxide were dissolved in one and a half litre of distilled water. One mole of granular aluminium was dissolved in this base solution, and the resulting solution filtered. The filtrate was acidified with iron free nitric acid to an incipient precipitation of aluminium hydroxide. The precipitation was then completed at room temperature with a stream of carbon dioxide. The precipitated hydroxide was washed with distilled water until the washings were neutral to litmus. The washed precipitate was transferred to a clean dry china dish and left in an air even at 110° for 12 hours.

(b) Preparation of chromium-aluminium oxide catalysts:

For this purpose, the procedure adopted was that of Bischens and Selwood, involving the impregnation of activated alumina with an aqueous solution of the requisite amount of chromium trioxide and subsequent reduction in situ in an atmosphere of hydrogen.

About 4.5g. of anhydrous chromium trioxide (Schering Kahlbaum) was dissolved in distilled water. To this solution about 16g. of \( \gamma \)-alumina in powder form was added and allowed to stand over-night. The chromic acid impregnated alumina was then filtered,

dried at 110° for 6 hours in an air oven and then pressed into cylindrical pellets, 4 mms. by 4 mms. The pellets were then placed in the dehydrogenation apparatus, calcined for 8 hours at 360°, and then reduced in a stream of hydrogen for 5 hours at the same temperature.

The chromium content of the catalyst was estimated by the method recommended by Eischens and Selwood, and it was found to be 3.9%.

Dehydrogenation:- 3-Carene (9.577g.) was passed over chromium-aluminium oxide catalyst (wt.7.92g; volume 12 ml; Cf. p. 164) heated to 400° at a liquid hourly space velocity (Cf.p.164) of 0.9600. The yield of the liquid products amounted to 88% on the wt. of 3-carene, with $n^\text{D} 1.4828$, 62-64% (by vol.) distilling between 170-180°/760 mm. The unsaturates in the liquid products were destroyed by agitation with twice its volume of 80% sulphuric acid for 4 hours, and the unaffected oil was separated and dried (yield: 75% on the wt. of 3-carene). This saturated oil had the following physical characteristics: $n^\text{D} 1.4946$, 71-72% (by vol.) distilling between 170-176°/760 mm., pale yellow colour and strong odour of cymene. The oxidation of 459 mg. of the saturated oil by

* The experimental arrangement is the same as that used for the investigation of the cracking of α-pinene (Cf. Section F Part II).

boiling 3 hours with a mixture composed of 6g. potassium dichromate, 10 ml. sulphuric acid, 15 ml. water and 20 ml. acetic acid gave 221 mg. of terephthalic acid and 209 mg. of isophthalic acid.

Further, the gases evolved during the catalytic reaction amounted to 1026 ml. and this was found to be hydrogen by micro analysis (Cf. p. 168).

**PART III- DISCUSSION:**

Attention has already been drawn to the fact that the published literature so far reports only p-cymene as the product of catalytic aromatisation of 3-carene. Theoretically, however, 3-carene can dehydrogenate with decyclisation at the C_6-C_7 and C_1-C_7 bonds to yield respectively p-cymene and m-cymene.

Now, by conducting the vapours of 3-carene over chromium-aluminium oxide catalyst, a saturated oil amounting to 75% on the wt. of 3-carene was obtained, and its physical properties suggested a high proportion of cymenes in it. The nature and quantity of the cymenes in this oil were determined by its oxidation with dichromate mixture to terephthalic acid and isophthalic acid, which must come respectively from p-cymene and m-cymene originally present in the saturated oil, and in amounts theoretically equivalent to 39% p-cymene and 27% m-cymene. Thus, theoretically, 66% of the saturated oil is accounted for as cymenes.
However, based on the value of terephthalic acid obtained by oxidation of pure p-cymene with dichromate mixture, (Cf. p. 95), the terephthalic acid yielded in the oxidation of the saturated oil would correspond to 46% p-cymene. Thus a minimum of 73% of the saturated oil is composed of cymenes, i.e. 54.7% on the wt. of 3-carene. The total percentage of the cymenes in the saturated oil is much higher, because in calculating the last-mentioned percentage of total cymenes i.e. 54.7% only the theoretical amount of m-cymene based on the isophthalic acid isolated from the oxidation of the saturated oil is taken into account.

The alternative route of estimating the cymene content based on the hydrogen liberated in the catalytic test, leads to a conversion amounting to 63% on the wt. of 3-carene, which is approximately 8 to 9% higher than the conversion evaluated on the basis of the dicarboxylic acids.

Thus, the aromatisation of 3-carene over chromium-aluminium oxide catalyst leads to the formation of p- and m-cymenes approximately in the ratio 3:2 (based on the theoretical amounts). That m-cymene was not the product of isomerisation of p-cymene under the influence of the catalyst at high temperature is shown by the fact that no m-cymene was obtained in the vapour phase aromatisation of terpineol with chromium-aluminium oxide catalyst under more drastic conditions (Cf. Section B, Part II).
PART IV: SUMMARY OF SECTION D:

(1) It is demonstrated that 3-carene can furnish simultaneously both p- and m-cymenes by vapour phase dehydrogenation. This conversion is unique because it is for the first time, in the vapour phase study of 3-carene that such a two-way aromatisation is experimentally realised. Moreover, so far, no other terpenoid has behaved like this over chromium-aluminium oxide catalyst to yield the two aromatics simultaneously.

(2) The chromium-aluminium oxide catalyst in which \( \gamma \)-alumina is the base, causes simultaneous formation of p- and m-cymenes from 3-carene in contrast to the chromium-aluminium oxide catalyst used by Guha et al and Sondhi (Cf.pp.136,137) which yielded only p-cymene. This leads to the conclusion that the mode of preparing the catalyst seems to be one of the important factors which decides whether the \( C_6-C_7 \), or \( C_1-C_7 \) and \( C_6-C_7 \) linkages of 3-carene get ruptured in the dehydrogenation.

(3) The presence of m-cymene in the catalysate proves that it is stable under the experimental conditions and does not seem to suffer irreversible isomerisation into p-cymene (Cf.p.137).

(4) The simultaneous formation of p- and m-cymenes from 3-carene establishes the structural relationship of the terpene to these aromatics.
(5) The vapour phase aromatisation of 3-carene into p- and m-cymenes is complementary to similar conversions achieved in the liquid phase.

(6) The yield of p- and m-cymenes obtained in this investigation is higher than that reported in the liquid phase aromatisations.