

SOME REACTIONS OF *p*-CYMENE

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P-CYMENE, 1-methyl-4-isopropyl benzene, is a common constituent of many essential oils. Sulfate turpentine is particularly rich in this hydrocarbon. Several methods mostly covered by patents are also available for its cheap production from readily available terpenes by vapour and liquid phase dehydrogenation.*

As a substituted benzene, *p*-Cymene is amenable to varieties of chemical transformations, thus constituting a potential raw material for the chemical industry. It is with this view, many of its more important oxidation, resin-forming hydration and thermal fission reactions are now discussed.

(A) OXIDATION REACTIONS

(i) *Electrolytic Oxidation*: Fitcher and Meyer¹ showed the intricate course of this reaction, having isolated 4-isopropyl benzaldehyde, 4-aceto-benzoic acid and terephthalic acid in one set, and 4-isopropyl-benzyl alcohol, 4-isopropyl- and 4-propenyl-benzoic acids, and probably diisopropyl-benzyl ether, in a second set of experiments.

(ii) *Vapour Phase Oxidation*: Senseman and Stubbs² isolated mostly 4-toluic acid (max. yield, 16.9% at 375° with sp. velocity 300 and 3-6 times the amount of air), besides terephthalic and formic acids, formaldehyde, carbon dioxide and water, using vanadium pentoxide deposited on porcelain as a catalyst. It appears >CH- group of the side chain is most readily attacked by this means.

(iii) *Liquid Phase Oxidation*: According to Stephens,^{3,4} oxygen attacks the isopropyl group of the hydrocarbon in the absence of any catalyst at 80°-100°, resulting in the loss of one methyl group as formic acid or carbon dioxide and water, with the formation of 4-tolylmethyl ketone. Oxidation of 1-methyl group also leads to 4-isopropyl benzaldehyde and benzoic acid.⁴ However, in presence of finely divided manganese dioxide or manganese 4-toluate,⁵ at 140-160°, 4-toluic, terephthalic and formic acids, formaldehyde, 4-tolylmethyl ketone, carbon dioxide and water are produced. Oxides of chromium, cobalt, iron, nickel and copper act as promoters. The non-formation of alcoholic products in this reaction is rather striking. On the other hand, Palmer and Bibb^{6,7} point out that oxidation in presence of a catalyst like a mixture of manganese and lead acetates, at 30°-50°, 40% conversion to 4-isopropyl benzoic acid^{6,8} is obtained. This is by far the best method for the production of this acid.

According to Tunghna Kuan,⁹ 4-tolylmethyl ketone (I) is obtained in 51% yield on oxidation with nitric acid (2 mols; $d=1.12$), but Hintikka¹⁰ who used 4 parts of nitric acid ($d=1.41$) and 5 parts of water, could isolate only 10% of this ketone (I) besides 67.5% 4-toluic acid, 5% terephthalic acid and 16.5% nitro-compounds. It may be noted that styrenes like 4-methyl, and 4- α -dimethyl styrenes could be readily obtained from (I) by appropriate chemical reactions,¹⁰ via the carbinols, but from a practical operative standpoint it would be economical to produce these styrenes and the carbinols directly from

p-Cymene (see under Thermal fission). In this connection the experiments of Palmer and Bibb⁶ are of interest. If oxidation by air is carried out at low temperatures below 50°, in presence of manganese and lead acetates, hydroxides or salts of a heavy metal of an organic acid as catalyst, α -dimethyl-4-tolyl carbinol and 4-tolylmethyl ketone (I) are formed⁸ which can be recovered after dehydration as the styrene and the ketone (I) by fractionation. All these products are of commercial significance. The ketone (I) is a good soap perfume and the styrene (4- α -dimethyl styrene) possesses analogous polymerising properties as the ordinary styrene, in yielding tough, colorless resins.⁶ The carbinol which has a higher boiling point than α -terpineol, possesses good wetting properties suggesting its substitution for pine oil when higher alcohol content is desired. The styrene itself can readily be obtained by dehydration in presence of active carbon or graphite,¹¹ and this forms polymers and co-polymers,^{12,13} by heat, cold con. sulphuric acid and benzoyl peroxide.

(B) RESIN FORMATION, HYDRATION AND THERMAL FISSION

(i) *Resin-forming Reactions*: Useful resins could also be obtained directly by chlorination of *p*-Cymene at temperatures above 100° in presence of Al, Fe or Zn, the cymyl chloride formed *in situ* undergoing a self Friedel-Crafts reaction, resulting in the formation of a dimer. The resins thus obtained however generally contain 10-30% chlorine (probably by nuclear chlorination and other causes).¹⁴

Varieties of resins can be obtained by previously incorporating other ingredients with *p*-Cymene. Addition of *o*-dichloro benzene gives a resin of higher chlorine content with added resistance to weather and water compositions. Inclusion of naphthalene produces a harder resin which is not readily attacked by petroleum distillates.¹⁴

These resins are insoluble in acids, alkali and ethyl alcohol and are not affected by hot 15% sodium chloride solution. Coating compositions derived from such resins could be used with advantage in marine work and chemical plants, in the treatment of railroad ties and telephone poles. Stains, varnishes, and lacquers have been prepared from these resins using *o*-dichloro benzene and *p*-Cymene as thinners. Satisfactory black, pliable coating composition can also be prepared without the use of extraneous pigments. These resins cannot be brought to the infusible state by heat and pressure treatment.¹⁴

(ii) *Hydration*: A simple, elegant and remarkable catalytic hydration of *p*-Cymene of great technical importance has recently been discovered by Schwartz.^{15,16,17} In essence, it involves the saturation of the three double bonds resulting in camphor in a rather unusual manner.

The catalyst recommended is a mercury compound, e.g., HgO or HgCl₂, or fatty acid salt, e.g., sodium stearate, and the reaction is preferably carried out in a mutual solvent, e.g., methyl alcohol, and at temperatures

* In this country from Indian Turpentine Oils.

above 35°, particularly at the boiling temperature. Modifications of the process consist in carrying out the reaction under 10 atmospheres pressure in the absence of solvent, and also in vapour phase.

(iii) *Thermal fission*: Cracking *p*-Cymene at 300°-450° with activated bleaching earths produce toluene and propylene,¹⁸ e.g., with 'tonsil' and at 420°, 60.5% toluene, besides 10% unchanged *p*-Cymene, saturated hydrocarbons (1.6%; b.p. 50°-60°, and 2%; b.p. >180°) and 25% gas (80% propylene) is obtained.¹⁹ Other methods^{20,21} cover the production of toluene and propylene using a catalyst comprising of alumina and silica.

Selective elimination of a methyl group from the isopropyl residue as methane has been effected by Ostromisslensky and Shepard^{22,23} by passing the hydrocarbon admixed with carbon dioxide through a tube at 650°: 40-50% yield of 4-methyl styrene is thus obtained. This is further investigated in detail by Breneck and Muller²⁴ who used iron, copper and aluminium catalysts. It is possible under suitable conditions to obtain 62% conversion into the styrene.

The selective dehydrogenation of *p*-Cymene into 4- α -dimethyl styrene achieved by Balandin and co-workers¹² is a recent contribution to the subject and marks an important advance. At 625°, with vanadium pentoxide as a catalyst, optimum conversion (63.4%) into the styrene takes place in presence of two mols of carbon dioxide. Improvements²⁵ of this process consist of reducing the partial pressure of *p*-Cymene by mixing with carbon dioxide and carrying out the reaction at reduced pressures and at lower temperatures, e.g., 500°.

Conclusion: The utilisation of *p*-Cymene in the past for the production of synthetic thymol and menthol is well known. As indicated above, varieties of products could be obtained from *p*-Cymene, and it is hoped that

this review will stimulate further investigations on the commercial utilisation of this important raw material for production of many useful substances.

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OSCAR EDWARD MEINZER*

IN the passing away of Dr. Oscar Edward Meinzer, the world has lost an eminent Geologist and a great authority on Ground-Water Hydrology. His famous treatise "The Occurrence of Ground Water in the United States with a discussion of Principles" published as Water Supply Paper No. 489 by the U. S. Geological Survey in 1923, and his numerous other papers on Hydrological investigations, specially on ground-water problems, contributed to the Governmental publications and Scientific and Engineering Journals, constitute a series of valuable references to Geologists and Hydrologists all the world over.

Dr. Meinzer was born on November 28, 1876, and hailed from a country farm in the State of Illinois. After a distinguished career at the College, he entered the U. S. Geological Survey in 1906 where he served for 40 years until his retirement in 1946. Through these long years of patient and able work, Dr. Meinzer has systematized the knowledge of the occurrence and principles of recovery through wells and springs of the supplies of water which are hidden in the rock formations. He was the leader in the development of ground water for useful purposes. He investigated the Geology and ground water resources in the arid valley regions of the

Western States of U. S. A. These valleys were then sparsely populated or desert areas, but have since become prosperous through irrigation from wells developed as a result of his investigations.

Dr. Meinzer was a member of numerous scientific societies. He was the past President of the Society of Economic Geologists, and the Washington Academy of Sciences, and other institutions. At the time of his death he was the President of the American Geophysical Union. He had been awarded the William Bowie Medal in 1943.

Dr. Meinzer was a man of varied interests. He was a student of Philosophy and maintained a searching interest in Religion.

It is reported that Dr. Meinzer was apparently in good health and spirits upto the day of his death, June 14, 1948, when he quietly passed away during an afternoon nap. Thus came the peaceful end of a great career.

M. B. R. RAO.

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