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PAPERS READ BEFORE THE CHEMICAL SOCIETY.

I.—*Isomeric Terpenes and their Derivatives.* (Part V.)

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§ 1. *Peppermint Camphor from Japan.*

OPPENHEIM has already shown (this Journal [1], xv, 24) that this substance is an alcohol (*menthylic alcohol*) of the form $C_{10}H_{18}OH$, and that by the action of dehydrating agents it splits up into water and a hydrocarbon, *menthene*, $C_{10}H_{18}$, bearing the same relation to terpenes that these do to cymene (*i.e.*, containing H_2 more).

Through the kindness of Mr. John Moss (Messrs. Corbyn and Co.), we received several ounces of crystallised Japanese camphor, together with the same amount of the so-called liquid camphor imported along with the crystals. The crystals were found by Oppenheim to melt at 36° , Mr. Moss observing 39° with the sample sent to us as the melting point, and 37.5° as the solidifying point. On attempting to crystallise the solid camphor from weak alcohol no crystals could be obtained, but an oil separated, which, on exposure to air (after separation by a tap-funnel from the aqueous liquid) became a mass of crystals. After several weeks' exposure to air, these crystals melted at 42° in a capillary tube, boiled at 212° (corrected; Oppenheim found 210°), and gave the following numbers on combustion :—

0.1945 gram gave 0.5445 CO_2 and 0.226 H_2O .

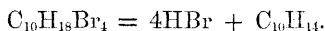
	Calculated.		Found.
C_{10}	120	76.92	76.35
H_{20}	20	12.82	12.91
O	16	10.26	—
	156	100.00	

These crystals were heated with about their own weight of zinc chloride, and the distillate, separated from water by a funnel, cohobated several hours with the chloride. The product was only very slightly resinized, almost the whole distilling below 170° . After cohobation with sodium, the greater part distilled between 164.5° to 165.5° (corrected), and gave the following numbers (Oppenheim gives 163° as the b.p. of menthene):—

0.1760 gram gave 0.5610 CO_2 and 0.2120 H_2O .

		Calculated.	Found.
C_{10}	120	86.96
H_{18}	18	13.04
		<hr/>	<hr/>
		138	100.00

Oppenheim has shown that when menthene is treated with two equivalents of bromine, a dibromide is formed which splits up with great facility into hydrobromic acid and bromomenthene, which again, by the action of caustic potash, forms a hydrocarbon, $\text{C}_{10}\text{H}_{16}$. Inasmuch as terpenes appear to be uniformly cymene derivatives, it seemed probable that when four equivalents of bromine act on menthene, a tetrabromide might be formed which would split up into cymene and hydrobromic acid, thus—



This is in fact the case, the action taking place without formation of much resinous matter, and the yield of crude cymene being nearly 60 parts per 100 of the menthene taken (theoretical 97 parts per 100). When bromine dissolved in aqueous potassium bromide solution is slowly added to menthene, combination takes place readily, with evolution of heat, but without the formation of more than traces of hydrobromic acid. At first the colour of the bromine rapidly disappears, but after about three equivalents have been added, the red colour disappears but slowly, and the combination with the last portions of bromine takes place only very slowly, being facilitated by heating the whole, some hydrobromic acid being thereby evolved. The resulting tetrabromide of menthene, or *tetrabromodecane*, readily splits up on heating, in accordance with the above reaction. By simple cohobation for a few hours until little or no fumes of hydrobromic acid escape, and distillation of the hydrocarbon (previously distilled off from a black resinous mass simultaneously formed) over sodium, nearly pure cymene is obtained. After further purification by treatment with sulphuric acid and cohobation with sodium, the cymene boiled almost wholly between 175° and 178° , exhibited all the characters of cymene, and gave the following numbers:—

0.2430 gram gave 0.7940 CO_2 and 0.2400 H_2O .

	Calculated.		Found.
C ₁₀	120	89·55	89·12
H ₁₄	14	10·45	10·98
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C ₁₀ H ₁₄	134	100·00	

This cymene yielded acetic and terephthalic acids on oxidation with chromic liquor, and furnished paratoluic acid with nitric acid (§ 2), and hence is identical with the cymene obtainable from the other bodies examined in the previous portion of these researches. Its production from menthene is of interest, as showing not merely a connection between the benzene hydrocarbons and the homologues of allylic alcohol (menthylic alcohol belonging to the series C_nH_{2n}O), but also as being an instance of the passage from a paraffin derivative (tetrabromodecane), to a benzene derivative, cymene, by a single action of decomposition.

The liquid camphor received from Mr. Moss yielded the following results. On fractional distillation a little distilled below 205°; the principal portion passed between 210° and 215°, whilst a smaller quantity distilled at 215°—220°, and a little remained non-volatile even at 300°; the portion distilling at 210°—215° yielded the following numbers on combustion:—

0·2185 gram gave 0·6120 CO₂ and 0·2420 H₂O.

	Calculated for C ₁₀ H ₂₀ O.	For C ₁₀ H ₁₈ O.	Found.
Carbon	76·92	77·92	76·38
Hydrogen...	12·82	11·69	12·30

from which it is evident that some substance less rich in hydrogen than menthylic alcohol is also present, the liquid being probably the solid camphor kept permanently dissolved in a liquid substance of composition C₁₀H₁₈O, analogous to and perhaps identical with citronellol from oil of citronella, which boils at about the same temperature. That this is so is rendered further probable from the circumstance that on cohobation with zinc chloride this distillate formed water, menthene, and liquids exhibiting no constant boiling point between 180° and above the limits of the mercurial thermometer. The menthene constituted about two-thirds of the product, boiled between 163° and 167°, and gave the following numbers after distillation over sodium:—

0·2425 gram gave 0·7745 CO₂ and 0·2850 H₂O.

	Calculated.	Found.
Carbon	86·95	87·10
Hydrogen	13·05	13·06

These numbers are quite consistent with the presence of a few per cents. of a terpene in the hydrocarbon examined, this latter being derived by dehydration from the substance $C_{10}H_{18}O$ in the original oil. The liquids of higher boiling point referred to above were similarly formed by more or less complete dehydration and polymerisation of this constituent; thus a fraction distilling at 245° — 255° contained carbon 83.5, hydrogen 12.0, whilst $3C_{10}H_{18}O - 2H_2O$ would require carbon 84.3 and hydrogen 11.7.

It was not found practicable to cause the crystallisation of the solid camphor from the liquid oil, even when a crystal of the solid body was dropped in, and the whole was kept some hours in a freezing mixture: it does not, however, follow from this that the constituent $C_{10}H_{20}O$ in the liquid oil was only isomeric with the solid camphor, as a very minute quantity of alcohol or hydrocarbon was found to prevent entirely the crystallisation of the solid camphor after it had once assumed the liquid state.

§ 2. On Cymene from Various Sources.

In former papers specimens of cymene from numerous sources have been examined by one of us, and the conclusion has been drawn that all the substances are identical with one another and with ordinary cymene, being a propyl- (or isopropyl-) methyl-benzene. It has, however, been suggested by Oppenheim (*Deut. Chem. Ges. Ber.*, vii, 625), that the experiments made do not exclude the possibility of some of the products being the corresponding diethyl-benzene, as this would also yield terephthalic and acetic acids on oxidation. We have, therefore, examined the action of nitric acid on some of these varieties of cymene, and find that in all cases *paratoluic acid* melting near 178° is formed. The hydrocarbons examined were boiled for 15—24 hours in a large flask, with an inverted condenser attached, with diluted nitric acid (1 part acid of sp. gr. 1.42 to 3 of water). On distillation in a current of steam, toluic acid passed over, more or less terephthalic acid remaining behind. By evaporating the distillate, after supersaturating with caustic soda, and adding nitric acid, a quantity of crude toluic acid was precipitated, amounting to from 25 to 60 per cent. of the cymene used; the actual quantity of toluic acid formed was always greater, it being difficult to distil over every trace. The crude acid thus obtained was then boiled for several hours with tin and hydrochloric acid to reduce any nitrotoluic acid present, and was finally recrystallised from boiling water after two or three successive solutions in ammonia and precipitations by hydrochloric acid. The following melting points and analytical numbers were obtained:—

- A. Toluic acid from cymene from hesperidene dibromide (hydrocarbon of oil of orange-peel).
- B. Toluic acid from cymene from myristicene dibromide (hydrocarbon of nutmeg oil).
- C. Toluic acid from cymene prepared from cajeput oil by phosphorus pentasulphide.
- D. Toluic acid from cymene from the dibromide of citronellol (oxidised constituent of citronella oil).
- E. Toluic acid from cymene from myristicol by phosphorus pentachloride (oxidised constituent of nutmeg oil).
- F. Toluic acid from cymene from absinthol and zinc chloride (oxidised constituent of wormwood oil).
- G. Toluic acid from cymene from tetrabromodecane from menthene (*supra*).

	A.	B.	C.	D.	E.	F.	G.
Corrected melting point in capillary tube	178°	177·5°	179°	178°	178°	176·5°	178°

A. 0·3330 gram gave 0·8650 CO₂ and 0·1770 H₂O.

B. 0·3350 " 0·8700 " 0·1820 "

C. 0·2640 " 0·6860 " 0·1450 "

D. 0·3195 " 0·8305 " 0·1735 "

F. 0·3125 " 0·8150 " 0·1730 "

G. 0·3045 " 0·7845 " 0·1685 "

Calculated.			Found.					
			A.	B.	C.	D.	F.	G.
C ₈	96	70·59	70·84	70·82	70·84	70·89	71·12	70·26
H ₈	8	5·88	5·90	6·04	6·10	6·03	6·15	6·15
O ₂	32	23·53	—	—	—	—	—	—
C ₈ H ₈ O ₂	136	100·00						

It is noticeable that the melting point of toluic acid has been given by different observers at various temperatures between 170° and 178°. With pure substances dissolving in ammonia to a *perfectly colourless* solution, we have uniformly found that the uncorrected melting point lies near 176° to 177°, giving with the thermometers used (4 for each observation) 178°—179° as the corrected value. Small quantities of colouring matter, &c., lower the melting point, and the presence of bromotoluic or nitrotoluic acid has the same effect.

It is also noticeable that whilst from the analytical numbers and boiling points of the cymenes used, together with their identical physical properties as observed by Dr. Gladstone, there was every reason to believe that each specimen was as nearly chemically pure as

such bodies can ever be obtained; nevertheless some specimens acquired a yellowish tint, more or less marked, on keeping in well-closed bottles for several months, whilst others remained colourless. The most coloured specimen examined was F, and this yielded a toluic acid exhibiting a lower melting point and a higher percentage of carbon than any other sample. In nearly every case, too, the percentage of carbon found in the toluic series is slightly *higher* than the calculated value.

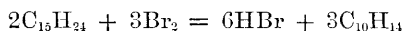
Taking into consideration the results obtained in this and the preceding four portions of these researches, together with those of Barbier, Oppenheim, Kekulé, Fittica, Beilstein and Kupffer, Riban, G. Williams, and others, it may be concluded that by the action of a large number of agents on terpenes and bodies related to them, *absolutely the same cymene results, this cymene being identical with the paramethylpropyl benzene* recently obtained synthetically by Fittica by acting with sodium on a mixture of normal propyl bromide and solid parabromotoluene melting at 29° .

Since at least *four* distinct isomerides of formula $C_{10}H_{16}$ can, by losing H_2 , produce the same cymene, and as only *three* such isomerides can be readily predicted from Kekulé's benzene formula, cymene being viewed as a 1 : 4 derivative, it results that in the production of cymene from at least one of these terpenes (and therefore possibly in the production of cymene from all its sources), the reaction is not so simple as would at first sight appear, but that it belongs to that class of reactions where "change of position" is said to occur, *i.e.*, in the symbolic representation of which, groups of symbols not otherwise affected must be made to alter their relative positions.

§ 3. On Clove-oil Hydrocarbons.

In order to see if polymerides of terpenes of the $C_{15}H_{24}$ series are capable of giving rise to cymene, a specimen of the hydrocarbon contained in clove oil, kindly presented by Professor Church, was examined. The corrected boiling point of this was found by Professor Church to be 253.9° , a number quite corroborated by our own observations. The vapour density of this substance clearly indicated that its formula is $C_{15}H_{24}$, *i.e.*, that it belongs to the series of sesquipolymerides of terpenes, or cedrenes, as they may be conveniently termed.

On treating this body with bromine, in quantity requisite for the reaction



combination ensued, a yellowish oily heavy liquid resulting. Much heat was evolved, but little or no hydrobromic acid was formed whilst the whole was kept cooled; on heating, however, torrents of hydrogen

bromide were given off. On distillation, a quantity of brown resinous matter was left, not volatile at 300° , whilst a liquid distilled over at a lower temperature. This was cohobated until the fumes of hydrobromic acid almost ceased to be evolved, and then mostly distilled between 240° and 270° , a little resin being left. No trace of cymene could be isolated by fractional distillation. The greater portion boiled between 250° and 260° , and after cohobation with sodium yielded numbers showing that hydrogen had been removed from the hydrocarbon by the bromine.

0.2170 gram gave 0.7035 CO_2 and 0.2190 H_2O .

	Calculated.		Found.
C_{15}	180	89.11	88.41
H_{22}	22	10.89	11.21
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	202	100.00	

Nitric acid acts energetically on the clove hydrocarbon, producing a yellow resinous mass. By boiling the hydrocarbon with diluted nitric acid, no trace of toluic or of terephthalic acid seems to be formed, and nothing could be obtained in a fit state for analysis from the products of the action.

§ 4. *On the Liquid Oil from Camphor Sublimation.*

Through the kindness of Dr. Armstrong, we received a quantity of the liquid which drops from the mass of camphor formed during the process of sublimation. On continued fractional distillation this separated into a liquid boiling between 170° and 180° , slightly impure camphor separating in crystals from the distillate at 210° — 220° , and resinous substances of higher boiling point, these latter being apparently formed chiefly by the action of heat on some of the constituents of the liquid.

The portion distilling at 170° — 180° was cohobated with sodium and then distilled almost constantly at 170° ; on combustion it gave numbers indicating that a terpene was the main constituent, a little of an oxidised body, probably of composition $\text{C}_{10}\text{H}_{18}\text{O}$, and analogous to or identical with cajuputol (which is not affected by boiling with sodium), being likewise present.

Calculated for $5\text{C}_{10}\text{H}_{16} + \text{C}_{10}\text{H}_{18}\text{O}$.		Found.
Carbon	86.21	86.04
Hydrogen	11.76	12.20

Apparently little or no cymene was present. On treatment with dilute nitric acid, a minute quantity of toluic acid was obtained (less

than 0·5 per cent.): hence not more than 1 per cent. of cymene could have been present in the fraction.

The fraction passing at 220°—230° gave numbers approximating to those required for $C_{10}H_{14}O$,

	Calculated.	Found.
Carbon.....	80·00	78·20
Hydrogen	9·33	9·25

whilst the resinous substances of higher boiling point appeared to be formed from this constituent and the $C_{10}H_{18}O$ body by partial dehydration; thus the portion distilling at 250°—260° gave numbers agreeing with $C_{30}H_{44}O_2$ or $C_{10}H_{14}O + 2C_{10}H_{18}O - H_2O$.

It hence results that the liquid camphor oil is a complex mixture, probably containing a hydrocarbon of the terpene series, a body having the composition of the hydrate of a terpene, $C_{10}H_{18}O$, and a liquid oil containing less hydrogen than camphor, together with much ordinary camphor.
