XXIX.—*Isomeric Terpenes and their Derivatives.*—Part II.—*On Cymene from Various Sources.*

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IN Part I it has been shown that the oil of nutmeg contains an isomeride of camphor, $C_{10}H_{16}O$ (first described by Gladstone, under the name of *myristicol*, and considered to be probably $C_{10}H_{14}O$); this substance is difficult to obtain pure, inasmuch as it occurs mixed with hydrocarbons of lower boiling-point and oxidised substances of higher boiling-point, from which it cannot be completely freed by fractional distillation, inasmuch as the myristicol itself alters by repeated distillation, becoming changed into polymeric modifications of higher boiling-point, and finally into a non-volatile resin.

* It has been shown by Prof. Williamson that chlorhydric sulphate and sodic nitrate yield nitrilic chloride.

§ 1. *Action of Phosphorus Pentachloride on Myristicol.*

When the purest myristicol that can be obtained (boiling at 212° — 218°) is dropped on well-cooled phosphorus pentachloride, a vigorous reaction takes place, much hydrogen chloride and phosphorus oxychloride being formed; the complementary product is decomposed by distillation, and can therefore only be obtained approximately pure. In one experiment, where elevation of temperature during the reaction was avoided as much as possible, a yellowish-brown liquid was obtained, which gave the following numbers on analysis, after washing with cold water to remove hydrogen chloride and phosphorus oxychloride, and drying over calcium chloride:—

0.275 gram gave 0.717 CO_2 and 0.225 H_2O

0.311 „ „ 0.220 AgCl

Carbon	71.1
Hydrogen	9.1
Chlorine	17.5
Oxygen (by difference)	2.3
	<hr/>
	100.0

No further action was exerted on this product by phosphorus oxychloride, whence it appears that the oxygen present was contained, not as myristicol, but as some other body not acted on by phosphorus pentachloride; on heating, much hydrogen chloride was given off, a hydrocarbon distilled between 170° and 190° , and a small quantity of a black resinous mass was left behind in the retort; this gave the following numbers, agreeing with the empirical formula $\text{C}_{40}\text{H}_{50}\text{O}_5$; it did not contain chlorine.

0.4355 gram gave 1.252 CO_2 and 0.328 H_2O

	Calculated for $\text{C}_{40}\text{H}_{50}\text{O}_5$.	Found.
Carbon	78.7	78.4
Hydrogen	8.2	8.4

Without doubt this resin contained the oxygen found as above in the chlorinated product, which, therefore, had the composition—

	Calculated.	Found.
Carbon	71.6	71.1
Hydrogen	8.7	9.1
Chlorine.....	17.7	17.5

Hence the action of phosphorus pentachloride on the camphor-

isomeride forming the chief constituent of "myristicol," is expressed by the equation—

which is perfectly parallel with the action of phosphorus pentachloride on alcohols generally.

The action of this reagent on camphor is, however, different (Gerhardt), being indicated by the equation

whence it appears that camphor is a substance not belonging to the same series of compounds as myristicol, the former being apparently an aldehyde, $\text{C}_9\text{H}_{15}\text{.CHO}$, the latter an alcohol (probably a secondary one), $\text{C}_{10}\text{H}_{15}\text{.OH}$. Gerhardt and also Pfaundler have further shown (*Ann. Chem. Pharm.*, cxv, 29), that this dichlorinated camphor derivative splits up by heating into hydrogen chloride, and a body, $\text{C}_{10}\text{H}_{15}\text{Cl}$ (also obtainable by treating camphor with less phosphorus pentachloride than that required to form the dichlorinated body); this derivative is only isomeric with the body of same composition derived from myristicol, being, when pure, a crystalline body melting at 60° .

Louguinine and Lippmann have shown (*Bull. Soc. Chim. de Paris* [II], vii, 374), that when this crystalline body is heated for some length of time, or repeatedly distilled at a very slow rate, it splits up (like the chlorides of secondary alcohols) into hydrogen chloride and a hydrocarbon containing the elements of water less than the original camphor; thus—

The hydrocarbon thus produced appears to be ordinary cymene (*vide infra*, § 3); the isomeric chloride, $\text{C}_{10}\text{H}_{15}\text{Cl}$, produced from myristicol as just described, undergoes precisely the same reaction with even greater ease, one or two distillations of the crude chloride sufficing to yield a distillate, which (after distillation over sodium) has all the properties of cymene. The hydrocarbon thus obtained boiled between 174° and 179° , principally at 176° — 178° (corrected). The numbers given on analysis and the investigation of its oxidation-products are given in §§ 9 and 11.

In one experiment where the myristicol employed was not wholly freed from lower-boiling terpenes, the action of phosphorus pentachloride gave rise to liquids which apparently were mixtures of the chloride, $\text{C}_{10}\text{H}_{15}\text{Cl}$, and polymerides of the terpene, $\text{C}_{10}\text{H}_{16}$, formed by the action of the hydrochloric acid set free during the reaction, or of

the phosphorus oxychloride thus produced; on distillation of the crude liquid, a resin, not volatile at 300°, was left in the retort; this gave—

Carbon		88.1	Hydrogen		11.3
„		88.2	„		11.3

indicating a mixture of $(C_{10}H_{16})_n$ and $(C_{10}H_{14})_n$, which would require carbon 88.9, hydrogen 11.1.

A polymeride, $(C_{10}H_{14})_n$, is described further on, obtained from camphor in an analogous way; Greville Williams also obtained a similar body (which he termed *paracymene*), together with ordinary cymene by the alternate action of bromine and sodium on caoutchouc (*Jahresbericht*, 1860, 495).

§ 2. Action of Zinc Chloride on Myristicol.

The production of cymene from camphor by the action of dehydrating agents, such as zinc chloride or phosphoric anhydride, has been long known from the labours of Delalande, Gerhardt, and others; in the case of zinc chloride, however, Fittig, Köbrich, and Jilke have shown (*Ann. Chem. Pharm.*, 145, 129), that the action is by no means solely that indicated by the equation—

A much more complicated decomposition also takes place, whereby a variety of other substances are produced simultaneously with cymene.

Myristicol was gently heated in a retort with about half its weight of solid zinc chloride; before the boiling-point was reached, an action was perceptible, and water distilled over; at 170° and upwards, a hydrocarbon passed over, and at 250° a yellow-brown non-volatile resin was left in the retort; this could readily be separated from zinc chloride by decantation and filtration while hot and semi-fluid; it gave the following numbers:—

0.331 gram gave 1.045 CO_2 and 0.313 H_2O .

		Calculated.	Found.
C_{20}	240	83.91	83.58
H_{30}	30	10.49	10.51
O	16	5.60	—
$C_{20}H_{30}O$..	236	100.00	

The hydrocarbon which distilled was found (after treatment with sodium) to boil at 173°—177° (corrected); on analysis it appeared to be cymene; the numbers obtained and the results of its oxidation by chromic solution are given in §§ 9 and 11.

Hence the action of zinc chloride on myristicol is expressed by the reactions —

The body $\text{C}_{20}\text{H}_{30}\text{O}$ is, perhaps, the ether of the alcohol $\text{C}_{10}\text{H}_{15}\text{OH}$ (myristicol), viz., $\left. \begin{smallmatrix} \text{C}_{10}\text{H}_{15} \\ \text{C}_{16}\text{H}_{15} \end{smallmatrix} \right\} \text{O}$; not impossibly, however, it may be a polymeride.

When the higher polymerides of myristicol are similarly treated, no cymene at all is formed; black resins result, one specimen of which contained carbon, 76·7; hydrogen, 8·2.

§ 3. *Cymene from Camphor by the action of Phosphorus Pentachloride.*

The experiments of Louguinine and Lippmann referred to above, were repeated in order to obtain another variety of cymene for comparison with the others; the product of the action of a slight excess of phosphorus pentachloride on camphor was heated in a flask with a long vertical tube attached as a condenser; for the first few hours hydrogen chloride was evolved; by-and-bye this ceased; the hydrocarbon was distilled off and digested in the same way with sodium; the body finally obtained appeared to be pure cymene, boiling at 175° — 178° (corrected). Louguinine and Lippmann also found the boiling-point to be 175° — 178° ; its subsequent examination and analysis are given in §§ 9 and 11.

Simultaneously with this cymene, a polymeride of cymene appears to be formed in small quantity; a viscid tar not volatile at 300° was left in the retort after distilling off the cymene formed by the splitting up of the body $\text{C}_{10}\text{H}_{15}\text{Cl}$; this contained carbon, 89·05; hydrogen, 10·40; the formula $(\text{C}_{10}\text{H}_{14})_n$ requiring carbon, 89·55; hydrogen, 10·45.

§ 4. *Cymene from Nutmeg Hydrocarbon (precontained).*

It has been already stated in Part I that, by the action of sulphuric acid on the mixture of hydrocarbons boiling at 163° — 164° , derived from oil of nutmegs by long-continued fractional distillation, the terpene present is polymerized and cymene is left unaltered; cymene thus obtained boiled at 173° — 177° (corrected); its investigation and analysis are described in §§ 9 and 11.

§ 5. *Cymene from Oil of Turpentine (precontained).*

It has already been stated in Part I that ordinary oil of turpentine, when distilled over sodium, yields a hydrocarbon which is not (as usually supposed) a single body of formula, $\text{C}_{10}\text{H}_{16}$, inasmuch as

cymene can be isolated from it by the treatment with sulphuric acid previously referred to. The analysis and investigation of this variety of cymene are described in §§ 9 and 11. The hydrocarbon obtained boiled at 174°—177° (corrected), the hydrocarbon from which it was isolated boiling at 156°—159°; the quantity obtained was but small, about 3 per cent.

§ 6. *Cymene from Hesperidene Dibromide.*

Greville Williams showed (*Jahresbericht*, 1860, 495), that by the alternate action of bromine and sodium on caoutchene and turpentine, a hydrocarbon was formed apparently identical with cymene.

Barbier has recently found (*Bull. Soc. Chim. de Paris* [2], xvii, 18), that by treating terpin (the so-called hydrate of terebenthene) with bromine in the proportion of two equivalents or slightly more of the second to one of the first, water is eliminated and a dibrominated compound, $C_{10}H_{16}Br_2$, formed; when heated, especially in contact with caustic potash, this breaks up into hydrobromic acid and cymene, thus—

Oppenheim has since found that the same dibromide is formed by the direct union of two equivalents of bromine with the hydrocarbon of turpentine oil; heat alone causes the production of cymene only to a small extent, but heating in contact with aniline produces a large quantity of cymene (*Deut. Chem. Ges. Ber.*, v, 94 and 628). Citrene (from lemon oil) also unites with bromine, giving a dibromide which similarly splits up into hydrogen bromide and cymene.

In order to see if hesperidene would yield the same products, two equivalents of bromine were cautiously added through a capillary tube, to well-cooled hesperidene; no hydrobromic acid was evolved unless the temperature was allowed to rise considerably by too rapid addition. On heating the resulting slightly yellowish brown liquid, torrents of hydrogen bromide were evolved, and at 170° and upwards a liquid distilled, finally leaving behind an inconsiderable amount of a viscid brown resin; the distillate appeared to consist of a hydrocarbon and an unstable brominated compound, as hydrogen bromide was copiously evolved on redistilling the distillate after thorough washing with cold water and drying over calcium chloride. After three or four distillations, almost the whole of the hesperidene used was converted into cymene of considerable purity, the yield being, even in roughly conducted experiments, over 80 per cent. of the hesperidene employed. After boiling *per ascensum* with sodium for some time to destroy the last traces of brominated compounds, a hydrocarbon smelling exactly

like cymene and boiling at 175·5 to 177·5 (corrected) was obtained, only a few drops coming over below and above these limits respectively.

The analysis and investigation of this cymene are given in §§ 9 and 11; as this cymene is identical with all the other known forms of that hydrocarbon, it is evident that the dibromide of hesperidene undergoes precisely the same kind of reactions as the dibromides of citrene and the turpentine terpene, viz. :

also that these three terpenes may all be regarded as *dihydrides of cymene*.

Not improbably the splitting up of the dibromide takes place in two stages, thus—

the unstable brominated compound above mentioned being the intermediate body, $\text{C}_{10}\text{H}_{15}\text{Br}$; it was, however, impossible to obtain any actual proof of this, inasmuch as analysis fails to detect whether the mixture obtained by the first distillation of dibromide is—

Cooling in a freezing mixture did not cause the separation of any solid body from the mixture.

Oppenheim states that by the action of chromic liquor on the dibromide of the turpentine terpene, bromine vapours are evolved, and terephthalic acid produced (not bromo-terephthalic acid as perhaps might be anticipated); by the action of chromic liquor on hesperidene dibromide, a resinous mass is produced which is only slowly attacked by the boiling chromic liquor, bromine vapours being evolved: by the complete oxidation of 50 grams of hesperidene dibromide, there were produced only a few decigrams of terephthalic acid, amounting to about $1\frac{1}{2}$ per cent. of the dibromide used: of this—

0·4055 gave 0·852 CO_2 and 0·137 H_2O .

		Calculated.	Found.
C_8	96	57·83	57·30
H_6	6	3·62	3·75
O_4	64	38·55	—
$\text{C}_8\text{H}_6\text{O}_4$	166	100·00	

It appears extremely probable that this small quantity was produced, not from the dibromide itself, but from a small quantity of cymene

present either formed by the splitting up of the dibromide by the heat evolved during its formation, or by the heat of the boiling chromic liquor; so that in all probability, hesperidene dibromide, like hesperidene itself, does not form terephthalic acid by oxidation: although, therefore, hesperidene is, like citrene and other terpenes, a dihydride of cymene, yet the relations of the hydrogen to the cymene are very different in hesperidene from what they are in the others, a circumstance that might perhaps be inferred from, and is certainly connected with, the difference in the amount of heat generated by the union of bromine with the terpenes (*vide* § 7), or by the action of sulphuric acid on these different isomeric bodies.

§ 7. *Cymene from the Dibromide of the Terpene of Nutmeg Oil.*

As has been shown in Part I, and in § 4 of this paper, the hydrocarbon boiling at 163° — 164° , contained in oil of nutmeg, is a mixture of a terpene (dissimilar from the terpenes of turpentine, lemon oil, and orange oil) with ten or twelve per cent. of cymene. When it is treated with two equivalents of bromine, combination takes place between this terpene and the bromine, forming a dibromide very similar in characters to the dibromide of hesperidene, and like it, splitting up by the action of heat alone into hydrogen bromide and cymene.

Two differences, however, are noticeable; in the first place, a much smaller yield of cymene is obtainable in this way, only about 55 per cent. of the hydrocarbon used being converted into pure cymene, and of this some 10 or 12 per cent. is precontained; the remainder becomes changed into brown or black resinous substances; secondly, the union of a given weight of bromine with the nutmeg hydrocarbon evolves much more heat than is produced by the combination of the same quantity of bromine with hesperidene; it was not, however, found practicable to obtain any very accurate calorimetric determinations of the actual quantity of heat produced in each case.

Without doubt this circumstance, together with the similar result noticed in the case of the action of sulphuric acid on these two terpenes (p. 551 of this volume), is intimately connected with the difference in boiling-point of the two terpenes (163° — 164° for the nutmeg terpene, 178° for hesperidene), and with the different chemical reactions undergone by them; *i.e.*, is intimately associated with the question of the nature of their isomerism. It would be of great interest to examine carefully the different amounts of heat generated by the combustion of equal weights of isomeric terpenes; but independently of the difficulty in the way of obtaining sufficiently accurate results to be of any use in investigating the character of the differences between such isomerides, the previous experiments indicate that it is

not improbable that many bodies supposed to be pure terpenes may really be mixtures, and that in particular small percentages of cymene may be contained in them; the presence of this hydrocarbon would of course vitiate the results.

It may be predicted with considerable probability that the heat of combustion of hesperidene will be found to be less than that of the nutmeg terpene, a result quite in harmony with Julius Thomsen's results (*Deut. Chem. Ges. Ber.*, v, 769). Thomsen finds that in the case of analogous compounds, the higher the "molecular weight," the less is the heat of combination, thus—

H ₂ . O	+ 68357	H . Cl	+ 22001
H ₂ . S	+ 4512	H . Br	+ 8440
H ₂ . Se	—	H . I	— 6036

As a rule, the higher the "molecular weight," the higher the boiling-point in comparable cases (*e.g.*, the well-known increase of boiling-point by about 20° for each additional CH₂ in truly homologous series), so that it appears not improbable that it may be a general rule that, *cæteris paribus*, the higher the boiling-point the less is the heat rendered sensible in the formation of a given compound, and therefore the greater is the "energy" of that compound.

It is well known that the greater the heat evolved in the formation of a compound, the more stable it is; thus metallic zinc decomposes water (as in the "couple" of Gladstone and Tribe), because more heat is evolved in the formation of ZnO than in that of H₂O; and for the same reason mercury displaces silver from its salts, copper precipitates mercury, and zinc copper, and so on. Hence it might be inferred that the compounds of hesperidene would probably be less stable than those of its isomerides of lower boiling-point, which seems to be the case at any rate with the dibromides, Oppenheim having found that the dibromide of turpentine (the hydrocarbon boiling at 160°—161°) is but little affected by heat, whilst as stated above the dibromide of hesperidene (b.-p. 178°) is readily split up into cymene and hydrogen bromide by simply heating it, the dibromide of the nutmeg hydrocarbon (b.-p. about 164°) having an intermediate stability.

The cymene obtained from the nutmeg dibromide boiled at 176°—178°; its analysis and the investigation of its oxidation products are given in §§ 9 and 11.

§ 8. Cymene from Cummin Oil.

Cummin oil was distilled whereby a distillate was obtained at 170°—250°, about 15 per cent. of a resin, not volatile at 300°, being left in the retort. This gave numbers agreeing with the empirical

formula, $C_{14}H_{17}O$, as it contains 83·35 p. c. carbon and 8·87 hydrogen. The distillate was agitated with a concentrated solution of sodium-hydrogen sulphite, whereby a thick magma of crystals was formed; this was pressed in folds of linen whereby the uncombined cymene was squeezed out, floating on the top of the liquors thus extracted. The cymene thus separated from the cuminic aldehyde also contained in the oil was treated with strong sulphuric acid, whereby much heat was evolved, the mixture becoming chestnut-coloured; water was added, and the viscid oil which floated to the top was removed and again subjected to the same treatment. On distillation part of the oily layer passed over at 175° — 180° , the remainder constituting a viscid liquid resin not volatile at 300° . This contained 81·95 p. c. carbon, and 10·13 hydrogen, whence it appears that the resin was formed by the dehydrating action of the sulphuric acid on the cuminic aldehyde not completely separated by the treatment with sodium-hydrogen sulphide.

The volatile hydrocarbon was boiled with sodium for some hours, it then distilled at $175\cdot5$ — $177\cdot5$ (corrected), only a very few drops passing over below and above these limits respectively; the total quantity obtained was less than 20 per cent. of the oil used, that obtainable in a pure state being about 15 per cent. The analysis and oxidation products of this sample are given in §§ 9 and 11.

Of all the processes tried for preparing cymene, that described in § 6 (heating hesperidene dibromide) gave by far the best result as regards quantity and purity of product and ease of preparation.

§ 9. *Analyses of the foregoing Varieties of Cymene.*

- A. From myristicol by action of phosphorus pentachloride—
 0·2255 gram gave 0·738 CO_2 and 0·221 H_2O ,
 0·2250 gram gave 0·729 CO_2 and 0·220 H_2O .
- B. From myristicol by zinc chloride—
 0·269 gram gave 0·875 CO_2 and 0·271 H_2O .
- C. From camphor by phosphorus pentachloride—
 0·2265 gram gave 0·7445 CO_2 and 0·220 H_2O .
- D. Pre-contained in nutmeg hydrocarbon distilling at 163° — 164° —
 0·3010 gram gave 0·9825 CO_2 and 0·295 H_2O .
- E. Pre-contained in oil of turpentine—
 0·2070 gram gave 0·675 CO_2 and 0·209 H_2O .
- F. From hesperidene dibromide—
 0·2625 gram gave 0·8595 CO_2 and 0·2540 H_2O .
- G. From nutmeg terpene dibromide—
 0·2515 gram gave 0·820 CO_2 and 0·244 H_2O .

H. Contained in cummin oil—

0·2500 gram gave 0·818 CO₂ and 0·243 H₂O,0·2010 gram gave 0·656 CO₂ and 0·196 H₂O.

Calculated.		Found.							
		A.		B.	C.	D.	E.	F.	G. H.
C ₁₀ ..	120 89·55	89·26	88·36	88·70	89·62	89·02	88·93	89·31	88·92 89·01
H ₁₄ ..	14 10·45	10·88	10·86	11·19	10·79	10·89	11·22	10·75	10·79 10·80 10·80
C ₁₀ H ₁₄	134 100 00								

§ 10. *Boiling Points of the foregoing varieties of Cymene (corrected).*

A.	B.	C.	D.	E.	F.	G.	H.
176-178	173-177	175-178	173-177	174-177	175·5-177·5	176-178	175·5-177·5

Noad found 171·5°; Gerhardt and Cahours 175°; Church 171° before treatment with sulphuric acid and 175°—176° after, and Warren 179·5° for cymene from cummin oil; whilst cymene from camphor by zinc chloride was found to boil at 173°—176° by Fittig Köbrich and Jilke, and is stated to boil at 177°—179° (Kekulé, *Lehrbuch*); that from phosphoric anhydride and camphor was found by Delalande to boil at 175°. Oppenheim found the cymene produced from the dibromides of citrene and terebenthene boiled between 176° and 179°; whilst Louguinine and Lippmann found the cymene obtained from the product of the action of phosphorous pentachloride on camphor boiled at 175°—178°.

§ 11. *Action of Chromic Liquor on the foregoing varieties of Cymene.*

All the above-described specimens of cymene were oxidised by a large excess of a mixture of 2 parts potassium dichromate, 3 sulphuric acid, and a bulk of water equal to that of the sulphuric acid; an inverted condenser being attached, boiling was continued until the liquid which dropped back appeared no longer oily, *i.e.*, until nothing but slightly acid water distilled; this required about 30 or 40 consecutive hours' boiling for quantities of 8 to 20 grams of cymene.

In every case terephthalic acid was produced; the acid was purified by solution in ammonia and precipitation by hydrochloric acid, and careful search was made in each case for isophthalic acid, but without success; the acid dissolved out by boiling water or alcohol and that obtained by boiling the barium salt with water and precipitating the dissolved part by acids, appearing in every case to be pure unaltered terephthalic acid. In several cases the resulting acid was analysed; when this was not done, the peculiar physical properties of terephthalic acid were carefully noticed. The following numbers were obtained:—

A. From myristicol by pentachloride of phosphorus: terephthalic acid obtained = 40 per cent. of cymene used—

0·4020 gram gave 0·845 CO₂ and 0·138 H₂O.

B. From camphor by pentachloride of phosphorus, about 35 per cent.—

0·2895 gram gave 0·617 CO₂ and 0·103 H₂O.

C. From turpentine oil by sulphuric acid, about 30 per cent.—

0·3775 gram gave 0·797 CO₂ and 0·135 H₂O.

D. From hesperidene dibromide, nearly 45 per cent.—

0·414 gram gave 0·878 CO₂ and 0·140 H₂O.

E. From dibromide of nutmeg hydrocarbon, about 25 per cent.—

0·3755 gram gave 0·801 CO₂ and 0·1345 H₂O.

F. From cummin oil, about 60 per cent.—

0·4000 gram gave 0·842 CO₂ and 0·137 H₂O.

Calculated.			Found.					
			A.	B.	C.	D.	E.	F.
C ₈	96	57·83	57·32	58·12	57 59	57·84	58·17	57·41
H ₈	6	3·62	3·81	3·94	3 97	3·76	3·98	3·80
O ₄	64	38·55						
C ₈ H ₆ O ₄ ..	166	100·00						

Hofmann found (*Ann. Chem. Pharm.*, xcvi, 197) that cymene from cummin oil yielded by oxidation with chromic acid an acid which had the characters of terephthalic acid, but to which he attributed the formula C₈H₆O₄. De la Rue and Müller (*Ann. Chem. Pharm.*, 121, 88), and Schwanert (*Ann. Chem. Pharm.*, 132, 258), found that this so-called *insolonic* acid was only impure terephthalic acid.

Fittig and Ferber found that the cymene formed from camphor by zinc chloride did not yield terephthalic acid by oxidation (Kekulé, *Lehrbuch*, ii, 542); De la Rue and Müller, on the other hand, found (*loc. cit.*) that terephthalic acid was produced by oxidizing this variety of cymene. These contradictory results, together with those obtained by Riche and Bérard (*Jahresbericht*, 1864, 531) which led Kekulé (*Lehrbuch*, *loc. cit.*) to regard the cymene from cummin oil as different from that obtained from camphor, may no doubt be explained by the observations of Fittig, Köbrich, and Jilke that camphor yields a very complex mixture of products by the action of zinc chloride, and consequently that the cymene thus obtained is exceedingly impure.

The chromic liquors obtained in the above experiments were distilled and the distillate neutralized by soda and evaporated to a small bulk; a quantity of sulphuric acid, insufficient to neutralize the whole of the sodium present, was then added and the whole distilled, the distillates being converted into silver salt by treatment with silver carbonate. Had any higher homologues of acetic acid been present they must have been contained in the distillate; no appreciable quantity, however, appeared to be present in any case. After drying over sulphuric acid in the dark, and finally at 100°, the silver salts gave these numbers, agreeing in each case with those required for acetate;—

- A. From myristicol by pentachloride of phosphorus—
0.795 gram gave 0.511 metallic silver.
- B. From camphor by pentachloride of phosphorus—
0.2025 gram gave 0.1315 Ag.
- C. From turpentine oil by sulphuric acid—
0.428 gave 0.278 Ag.
- D. From hesperidene dibromide—
1st specimen, 0.3935 gave 0.2540 Ag.
2nd specimen, 0.509 gave 0.3285 Ag.
- E. From dibromide of nutmeg terpene—
0.623 gave 0.4005 Ag.
- F. From oil of cummin—
0.430 gave 0.278 Ag.

Calculated.			Found.						
			A.	B.	C.	D.		E.	F.
C ₂ H ₃ O ₂ ..	59	35.32	64.27	64.92	64.95	64.52	64.54	64.29	64.65
Ag	108	64.68							
C ₂ H ₃ AgO ₂	167	100.00							

In the other cases, where an analysis was not made, the qualitative reactions of acetic acid were obtained.

Oppenheim has found terephthalic and acetic acids to be formed by the oxidation of the cymene from turpentine dibromide and that from citrene dibromide; but he also observed the formation of small quantities of camphor formed by the reaction—

This substance was carefully looked for in each of the above cases, but was not found in any one instance.

§ 12. *Physical Properties of the foregoing Varieties of Cymene.*

In odour the eight varieties of cymene described above were indistinguishable one from another.

Dr. Gladstone has kindly determined the specific gravities, refractive indices, and dispersive powers of the above-described specimens of cymene, and finds that the differences are in no case greater than those usually noticed in different preparations of the same substance, such differences being due to error of observation and adhering traces of impurity. In all cases the numbers obtained approximate closely to the following mean values:—

Specific gravity.....	0·86
Refractive index	1·48
Dispersion.....	0·035

§ 13. *Conclusions.*

The foregoing results, summed up in §§ 9 to 12, indicate that there is but one variety of cymene produced from and existing in the bodies experimented with; this boils at 176° to 177°, and yields by oxidation terephthalic acid (in quantities much less than those theoretically obtainable) free from isophthalic acid; acetic acid free from higher homologues is also produced.

The production of terephthalic acid from cymene by oxidation shows that *two* "lateral chains" are present; and as toluic acid is also obtainable from cymene, one of these chains must be methyl (since toluic acid gives rise to methyl-benzene = toluene). Cymene therefore is either a methyl-propyl-benzene or a methyl-isopropyl-benzene.

If terephthalic acid be regarded as a 1 : 4 benzene derivative, there are but three formulæ attributable to bodies which can form cymene by loss of H₂, viz. :—

(where it is not stated whether Pr = ordinary propyl or isopropyl).

Four bodies are, however, now known which are apparently homogeneous and different substances, and yielding the same cymene by removal of H₂, viz. :—

The terpene of turpentine oil	} Williams, Barbier,
„ „ lemon „ = citrene	
The terpene of orange oil = hesperidene	} Oppenheim.
„ „ nutmeg „	
	} Wright.

Hence it must be supposed either that terephthalic acid is not a 1 : 4 dicarboxyl-benzene, or else that one at least of these hydrocarbons is really the dihydride not of a 1 : 4, but of a 1 : 3 or a 1 : 2 methyl-propyl-benzene, the radicals methyl and propyl altering their mutual relations to one another during the elimination of the H_2 , and finally arriving at the 1 : 4 position.

Whatever may be the actual character of the process thus symbolically indicated, there can be little doubt that it corresponds to the performance of "internal work" of some kind, and therefore that a change of this kind is probably coincident with the evolution of a quantity of heat less than that which would be produced by the removal of H_2 from the hydride of a 1 : 4 compound; if, therefore, it were possible to estimate the quantity of heat involved in the reactions—

some light might be thrown on the subject of the "structural" formula of the terpenes; unfortunately such determinations appear to be impracticable.

If terephthalic acid be viewed as a 1 : 3 benzene derivative, 6 formulæ exist indicating the dihydrides of cymene, and if as a 1 : 2 derivative, there will be 6 other formulæ, viz. :—

So that if it be supposed that the methyl and propyl groups can alter their mutual connections during the removal of H_2 , there are altogether 15 different possible formulæ for dihydrides of cymene.

Postscript.—While this paper was being written, Riban communicated to the Chemical Society of Paris a paper (reported by Henninger in the *Berichte* of the Berlin Chemical Society, 1873, p. 199), wherein he states that he has obtained cymene from turpentine oil by treating it with sulphuric acid. Riban, however, appears to consider

that the cymene is produced by the removal of H_2 from $C_{10}H_{16}$, the sulphuric acid being simultaneously reduced to sulphurous acid. The writer, however, considers that the cymene is *precontained as such* for the following reasons.

1st. The analytical numbers obtained (Part I) with the hydrocarbon boiling at 163° — 164° from nutmeg oil showed that there might be present a certain quantity of cymene without its presence being detectable by ordinary combustion; whilst the fractions boiling at 175° — 177° , 177° — 179° certainly contained cymene, which would render it next to impossible that a fraction boiling at only 10 or 12 degrees lower should be wholly free from that constituent. Hence the cymene obtained from the 163° — 164° distillate was almost certainly precontained. If nutmeg oil contain cymene ready formed in addition to terpenes, the latter being in great excess, the same might be the case with other analogous bodies, *e.g.*, turpentine.

2nd. Both nutmeg oil and turpentine yield terephthalic acid by oxidation, whilst hesperidene does not give a trace of that substance. By subjecting hesperidene to the treatment with sulphuric acid above described, no trace of cymene is obtainable, whilst both the other oils yield cymene by this process: hence it is highly probable that the terephthalic acid is derived in these instances (and in other analogous ones) from cymene precontained in the oils, and not from the terpene present. The possibility of hesperidene having a constitution of a kind utterly dissimilar from those of the nutmeg and turpentine terpenes, is negated by the experiments described above, whereby it is shown that hesperidene and the nutmeg terpene are (like citrene and the turpentine terpene according to Oppenheim) *dihydrides of the same cymene*.

3rd. The production of sulphurous acid, which undoubtedly takes place when terpenes are mixed with strong sulphuric acid, not improbably arises from the further action of the acid on the terpene polymeride formed; and although it is conceivable that this action might generate cymene, yet the production of this substance in this way is improbable, inasmuch as the action seems one of entire destruction, dark brown and black humus-like substances being formed. Hesperidene thus treated, yields much black humus-like substance, together with a large amount of sulphurous acid, but no trace of cymene. When the mixture of acid and terpene is kept cool, and the terpene added slowly, the formation of sulphurous acid and of black humus-like products, is much less than when the mixture is allowed to heat; by very cautiously working, the writer has succeeded in isolating cymene from oil of turpentine without the formation of more than inconsiderable quantities of sulphurous acid.