STUDIES

IN

THE TERPENES AND SESQUITERPENES.

by

JAMES SWORD, M.A., B.Sc., A.I.C.

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STUDIES IN THE TERPENES AND SESQUITERPENES.

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Part I.

Part II.

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Part I.

(1) A Critical Study of the Nature of Cedrene.

A Critical Study of the Nature of "Cedrene".

Although one of the first Sesquiterpenes to be discovered, the constitution of Cedrene still remains unexplained. It is, in fact, doubtful whether a sample of pure Cedrene has ever been handled, for it is the opinion of the writer that Cedrene is not one,,but a mixture of hydrocarbons. The earlier authors use the name Cedrene in a somewhat wider sense than it is now, as the existence of such Sesquiterpenes as Caryophyllene and Cadinene were at the time unknown. J.H.Gladstone [J.C.S., 1886, *49*, 609] refers to Cedrenes from Cloves, Rosewood, Cubebs, Calamus, Patchouli, and Cedar; referring to the last as especially representative of the name. As the oils from the other sources have been more carefully examined and their constituents separated, new names have been coined, and the general use of the term Cedrene abandoned until it is now used to denote that hydrocarbon found in the oil of Cedar Wood (*Juniperus Virginiana*) which boils at 124-126°/ *12mm*. It is probable that the term will require to be still further restricted.

There has not yet been established any satisfactory criterion for this hydrocarbon, for although it combines with bromine and the halogen acids, the compounds are too unstable to be isolated; nor do the oxides of nitrogen or nitrosyl chloride give any better result [Chapman, J.C.S., 1896. *11*, P. 140]>. The physical constants of the hydrocarbon, as recorded by various investigators, vary somewhat, as the following table shows:-

Constants of Cedrene as recorded by different investigators.

	Boiling Point		Density		Specific Rotation		Refractive Index.	
	Temp.	Press.	d_t^t	Temp.	$[\alpha]_D^t$	Temp	n_D^t	Temp.
A	261-262°	760 mm.	0.9359	15°	-60°		1.5015	
B	131-132°	10 mm.			-47°54'			
C.	124-126°	12 mm.	0.9354	15°	-55°		1.50233	
D.	122-124°	10 mm.	0.		-55°	15°		
E.	129-131°	17 mm.	0.9822	28.6°	*-64.84°	19.5°	1.4995	25.8°
			0.9390	15°			1.50432	15°

(Hg green light *)

References:-

A. Chapman, J.C.S., 1896, *11*, P. 140.

B. Rousset, Bull. Soc. Chim., 1897, *17*, (3), 485.

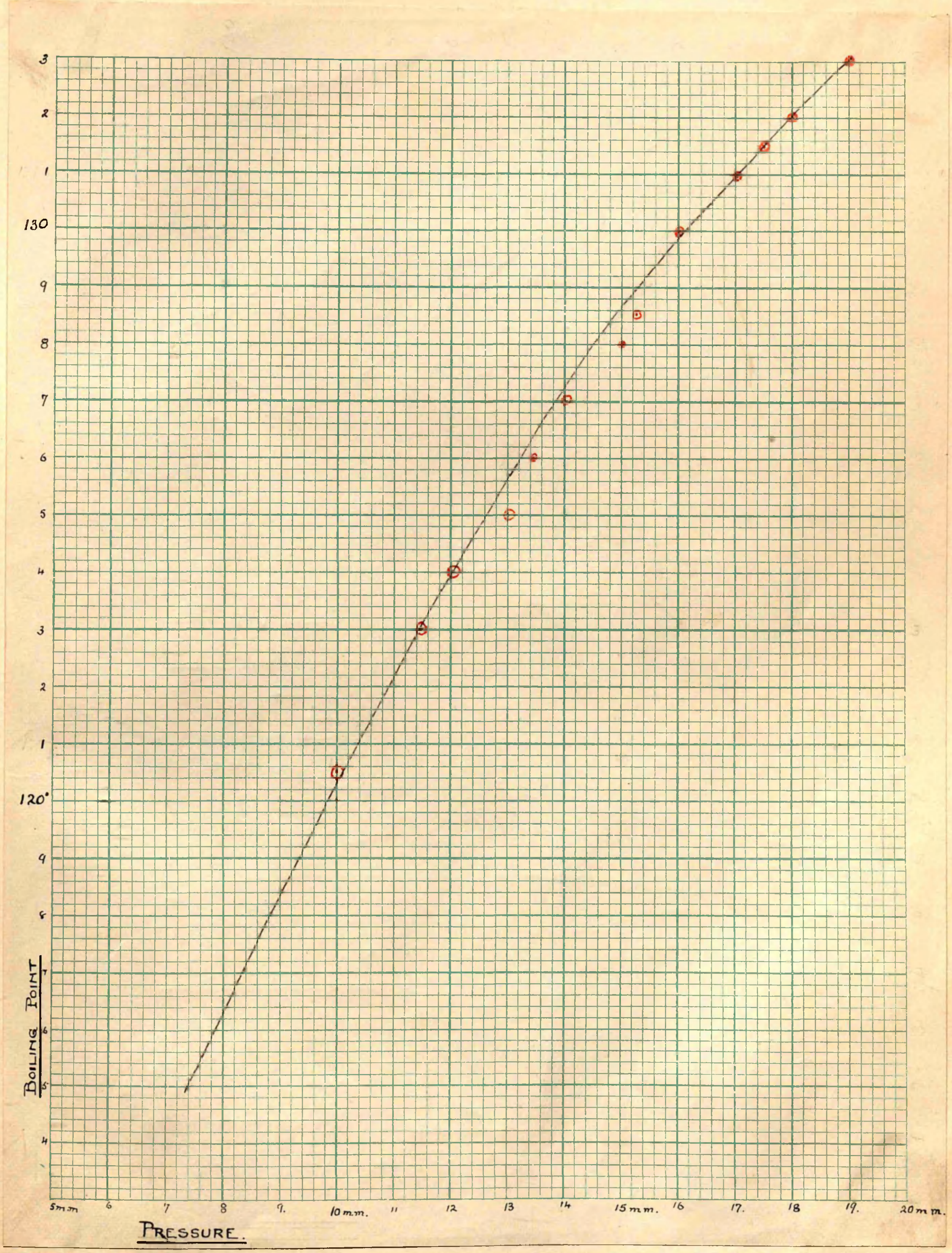
C. Semmler and Hoffmann, Ber., 1907, *40*, 3519.

D. Sword ,

E. Sword,

The lack of a common basis of comparison, so familiar in the records of physical constants, is evident here, as again on p.15 The reason is obvious. Reduced pressures are usually obtained by means of a water pump, with the result that the pressure obtainable on any day is dependent on the temperature of the tap water and the air at the time of observation. Thus boiling points are seldom recorded at the same pressure, nor densities and refractive indices at the same temperature. As in the above table, it is not unusual to find a refractive index recorded to the fifth decimal and the temperature of the observation omitted altogether: such a value is, of course, useless. As Cedrene gives no derivatives through which it can be purified, the only criterion of its purity is necessarily based on its physical constants. This being the case the necessity of having a common basis for the comparison is imperative,- a point which investigators would appear on occasion to have overlooked-. It would certainly appear that, before making the rather daring claims discussed on p.16, a much fuller record of constants, and a closer agreement between them would be necessary. The writer made it his first study to record the ~~the~~ constants of the hydrocarbon in such a way that they could be compared with any others at any temperature and pressure within the usual limits of working. A graph of the boiling points at different pressures will be found on p.4 a table of refractive indices at different temperatures on p50 one of changes in boiling point at very low pressures on p47

Graph showing Changes in Boiling Point corresponding to Changes of Pressure.



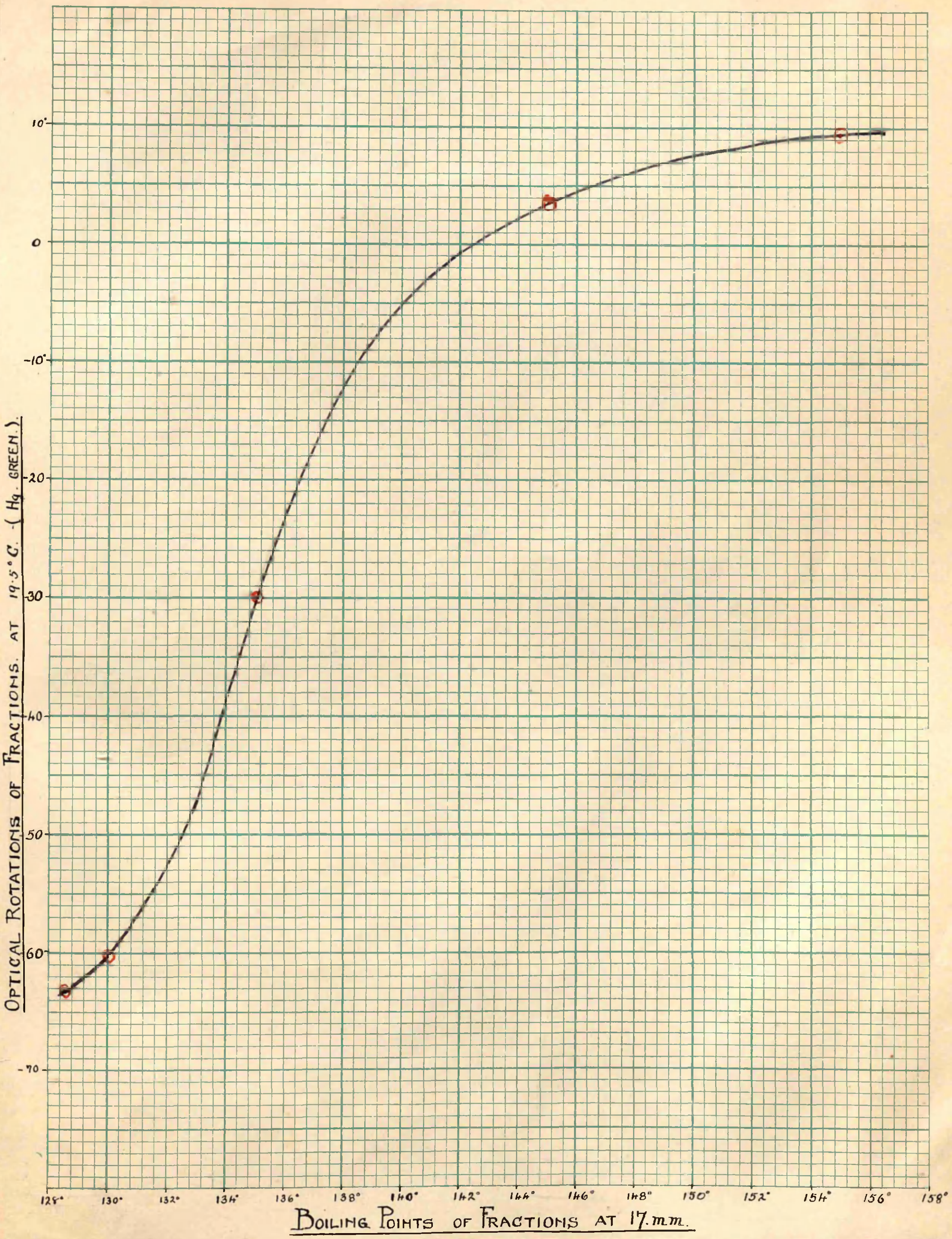
It would appear that the boiling point recorded by Rousset p.2.B, was in error, as it differs by 10° from that of any other observer; moreover, Semmler repeated Rousset's work using Cedrene as described by him p.2.C, and obtained, in the main, the same products. It was most probably an error caused by a faulty manometer, in which case, using the graph on p.4. the reading would be 131-132°/ 18mm.

As a consideration of the results of other chemists led the writer to suspect that Cedrene was not an individual hydrocarbon, he recorded not only the constants of the accepted fraction but also those of the preceding and subsequent fractions. A graph of the boiling points of the the various fractions against their refractive indices is shown on p.7, and one against their specific rotations on p.6. Tables of the boiling points, refractive indices, densities molecular refractivities, and specific rotations appear on pp. 48, 49, 50, 51, and 52 : a consideration of these shows that the possibility of this hydrocarbon being a mixture of isomers is a very real one. The very gradual changes in all the constants with rise in boiling point makes this conclusion almost inevitable.

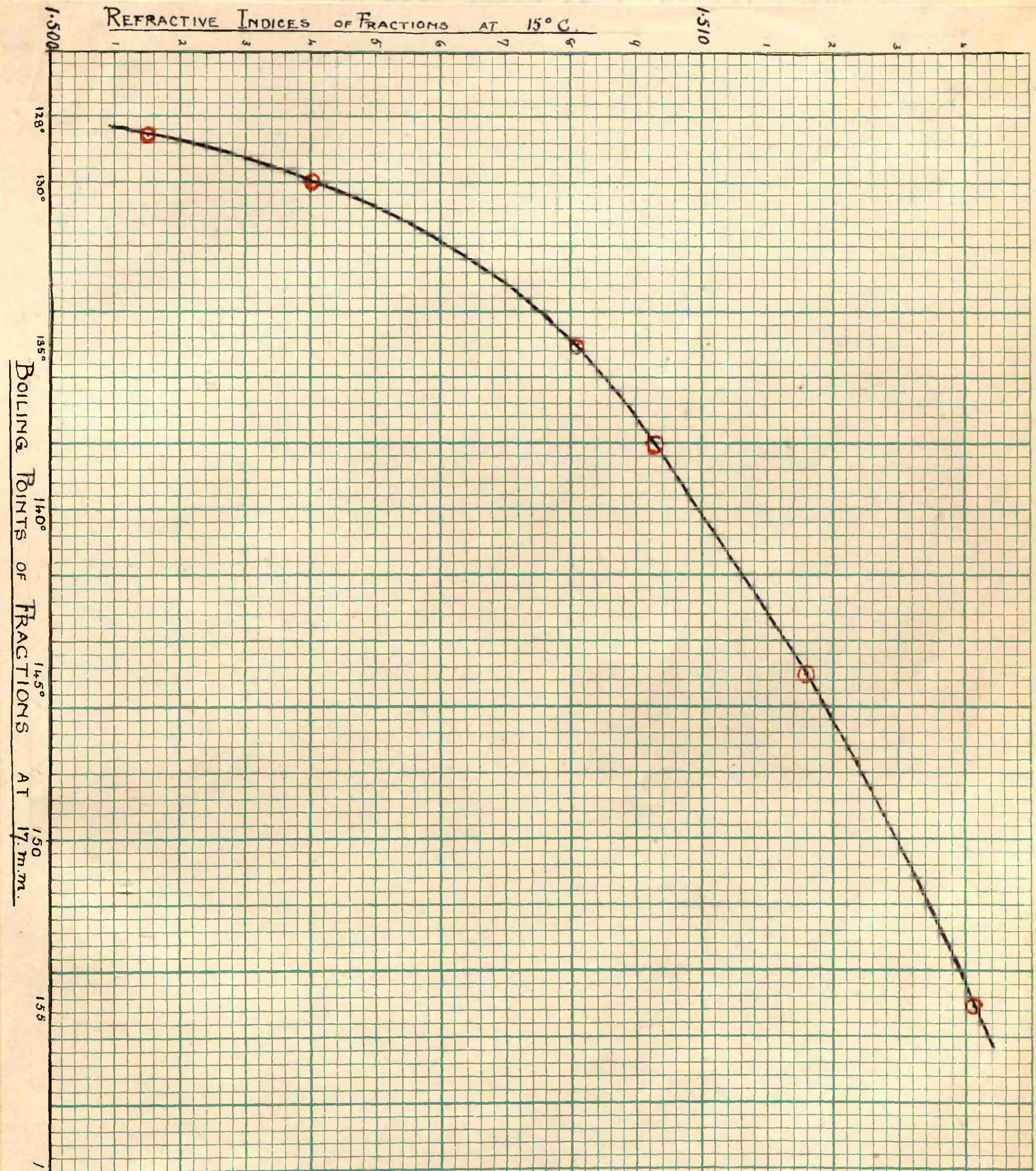
Evidence that 'Cedrene' is a mixture of isomers.

In the sample of 'Cedrene' supplied to the writer by Messrs W.J.Bush & Co Ltd, there was found a fraction boiling about 1° below the main fraction, and another fraction boiling about

@Graph showing Changes in Optical Rotation of the Fractions of crude Cedrene.



Graph showing Changes in Refractive Index of the Fractions of crude Cedrene.



4° above it. If the curves on pp. 6 and 7 be examined it will be found that in both there is a rapidly changing gradient round 130°/17 mm. or 123°/12 mm. This certainly shows that round that boiling point is to be found the most definite fraction of the natural oil, but the very gradual gradient shows that this is only a comparative term, and that even the most definite fraction contains more than one hydrocarbons. It would appear that the isomers have boiling points which are very slightly different. Even the most careful fractionation might fail in such a case to effect a separation. If the hydrocarbon is indeed a mixture of isomers the repeated failures to prepare any crystalline derivatives are explained.

If the work of other workers be examined in this light their results will be found to confirm this view, although hitherto apparently overlooked.

Although never satisfactorily proved, it has always been assumed that Cedrene has one double linkage in its constitution. from physical data. In his investigations of the refraction and dispersion of a very large and varied selection of organic substances [J.C.S., 1884, *45*, T. 264: 1891, *59*, T. 290] J.H.Gladstone obtained the following values for Cedrene (using the formula $\frac{n_A - 1}{d}$) for the specific rotation, and values for the calculation from the chemical formula detailed in these papers.)

Mol. refraction 108·52. (calc. for one double bond 108·4)
Mol. dispersion 5·35 (calc. 5·36)

Chapman, however, was unsuccessful in his effort to identify Cedrene by means of its hydrochloride or dibromide. A few years later Rousset repeated the work [Bull. Soc. Chim., 1897, *17*, 485], and, finding the same difficulties, tried to estimate the extent to which addition had taken place by estimating the chlorine in the chilled solution immediately after passing in the HCl gas. He found that only 60% of the amount of HCl necessary to saturate one double bond had been added. In the case of bromine he found that the reaction went rapidly at first but soon slowed down, and long before the necessary amount had been added HBr was liberated. The writer repeated this, using both chloroform and carbon tetrachloride as solvents, and found that the first 10% or so reacted instanter, after which the slowing down set in, in a way which indicated that there were at least two substances under treatment, the one present in smaller amount having an ordinary ethylenic linkage, the other having an unsaturation of a more complicated nature which was made unstable by the addition of a halogen or halogen acid

Again, potassium permanganate is a very reliable oxidising agent, giving as a rule a yield of oxidation product bearing a satisfactory relation to the theoretical yield; with Cedrene the yield of glycol was only 10-15%, the main products being ketonic in structure. There would seem to be more than a chance agreement between these two reactions: it would indeed appear that again the portion having the ethylenic bond had given an almost quantitative yield of glycol, the other portion again reacting in an altogether unusual manner.

A similar result was obtained by S.T.R.S.Mitchell in this laboratory when studying the reaction of perhydrol on Cedrene: only a small yield of glycol (5-10%) was obtained, the main product in his case being an alcohol. The same cause would explain the result as in the case of the permanganate oxidation.

In the paper cited above Rousset states that Cedrene does not give an alcohol $C_{15}H_{25}OH$ when treated with H_2SO_4 in glacial acetic acid. The writer repeated this and found that the recovered hydrocarbon had entirely lost the smell of Cedar Wood, its boiling point, while practically the same, showed in some of the experiments indications of a lower boiling fraction. The optical rotation had increased. (see pp.72,73) It would appear that the sulphuric acid had attacked the isomer to which the oil owes its characteristic smell, leaving the more stable isomer of higher rotation. There is the further possibility that the treatment produced a new isomer.

Thus every investigation furnishes another evidence of the heterogenous nature of Cedrene.

The Constitution of Cedrene.

For information regarding the constitution of Cedfene we are almost entirely dependent on deductions from the physical constants. An examination of the various hydrocarbons of the terpenes shows that the densities of the monocyclic terpenes , Limonene, Sylvestrene, Terpinene, Phellandrene, etc, range from 0·847 to 0·860 at 15°, and that the densities of the bicyclic terpenes such as the Pinenes, and Camphene range from 0·863 to 0·875 / 15°. In the sesquiterpenes the densities of Zingiberene and Bisabolene are, respectively, 0·875 and 0·881 / 15°. These are thought to be the only representatives of monocyclic sesquiterpenes. The densities of Cadinene, Caryophyllene, Selinene, Humulene, β.Santalene, Atractylene, Caparrapene, and Guagene range from 0·900 to 0·924 / 15°: these are all thought to be bicyclic; in the case of Cadinene the constitution is almost established. The densities of Cedrene, Clovene, Heerabolene range from 0·935 to 0·943: these are thought to be tricyclic. As a consideration of the molecular refractivities divides them into the same classes,.. the values for the three classes being:- monocyclic 67·76, bicyclic 66·15, and tricyclic 64·45...there is good reason to believe that this classification is correct. While the terpenes can be divided into two classes by their boiling points...bicyclic 150-165°, monocyclic 170-180°, there is no similar division as yet apparent in the sesquiterpenes whose boiling points all lie between 260° and 270°, and apparently irrespective of constitution. From a consideration of its physical constants alone Cedrene appears to be a tricyclic sesquiterpene having one double bond somewhere in the molecule.

The results of investigations of a purely chemical nature lead to much less certain conclusions, the unusually difficult nature of the task being shown by the uncertainty which accompanies the results of every research on this hydrocarbon. Chapman's work has already been mentioned. His results were negative in as much as he failed to prepare any addition compound, but positive in as much as a reaction undoubtedly took place: nor have later experimenters been more successful. The assertion that Cedrene has one unsaturation therefore remains unproved chemically. Chapman, in the same paper, further concluded that the hydrocarbon he obtained from Santalal, the aldehyde $C_{15}H_{22}O$, was not identical with the natural Cedrene, as its boiling point is two degrees higher, and although the densities are the same, the specific rotation is +5°45' while that of Cedrene is -60°. Other Chemists have considered such disagreements as no obstacle in proving that the Cedrenes obtained by reducing Cedrol, Cedrenol, and ΨCedrol were all identical with the natural Cedrene(see p18). The uncertainty regarding the boiling point of Rousset's sample has been mentioned, but that is not all. On oxidising his

Cedrene with chromic acid he obtained a ketone, Cedrone $C_{15}H_{24}O$, which, on reduction with sodium, gave an alcohol iso-Cedrol $C_{15}H_{26}O$. The ketone reacted with sodium hypobromite and potassium iodide to give iodoform, indicating the presence of the group $CH_3.CO-$. On repeating this work Semmler and Hoffmann state [Ber., 1907, *40*, 3519] that chromic acid gives Cedrone $C_{15}H_{22}O$, which, on reduction gives an alcohol not iso-Cedrol but dihydro-iso-Cedrol $C_{15}H_{26}O$, and that Cedrone contains the group$-C{=}C.CH_3CO.C-$. They do not deny that it gives the iodoform reaction, but appear to explain it by the note that crude Cedrone contains another ketone.

In the same paper are described the actions of potassium permanganate and ozone on Cedrene. The former gave the glycol $C_{15}H_{26}O_2$ referred to on p.10, a keto-aldehyde or diketone, $C_{15}H_{24}O_2$, and a keto-acid $C_{15}H_{24}O_3$; the latter gave an indifferent product $C_{14}H_{24}O$ or $C_{14}H_{22}O$ (a ketone), the keto-aldehyde $C_{15}H_{24}O_2$ already mentioned, and the ketonic acid $C_{15}H_{24}O_3$. As the formation of this ketonic acid by the decomposition of the ozonide is used by these authors as the infallible proof of Cedrene it is described by them in detail It is characterised in the first place by its semicarbazone and its methyl ester: it is readily oxidised by permanganate to the corresponding dicarboxylic acid $C_{15}H_{24}O_4$, ~~which in turn~~ which in turn can be characterised by its melting point and its methyl ester.

In the oil of Cedar Wood there is usually found along with Cedrene, a tertiary alcohol Cedrol. By dehydrating this alcohol with phosphorus pentoxide Walter prepared a hydrocarbon which he called Cedrene [Lieb. Ann., 1841, *39*, 247]. By a similar reaction but using formic acid as dehydrating agent, Semmler and Spornitz ? obtained a hydrocarbon b.p. 112-113/7 mm., $[\alpha]_D$ -85°. This they conclude must be Cedrene since it gives the same keto- acid. In some classes of organic substances these facts might be accepted as conclusive proof, but in a class of substances in which the number of isomers is so large, the lower boiling point, the much higher rotation and the absence of other physical constants would make the assumption appear rather daring. ?

In addition to the crystalline Cedrol, a primary alcohol was discovered by Semmler and Mayer [Ber., 1912, *45*, 786] which they named Cedrenol. Although a small fraction it is an invariable constituent of the oil of Cedar Wood. It is a liquid, is tricyclic and contains one double bond. On reducing Cedrenyl chloride with sodium and alcohol the authors obtained a hydrocarbon b.p. 117-130° / 17mm., $d^{20°}$ 0·931, n_D, 1·5081, $[\alpha]_D^{20°}$ -3° to +13°. The refractive index is useless without the temperature of observation; and with a boiling point ranging over 13° it would seem even more daring to assert that this also is Cedrene, yet it yields the keto-acid on oxidation with ozone, and this the authors consider sufficient.

The same chemists isolated a third alcohol from the oil of Cedar wood; this they called Ψ.Cedrol because they found it to be chemically identical with Cedrol (gave the keto-acid) and physically isomeric with Cedrol, [Ber., 1912, *45*, 1384]. On reduction with zinc dust in a sealed tube, it yielded Cedrene and dihydrocedrene. The Cedrene was again identified by means of its keto-acid, the dihydrocedrene by its combustion as it did not agree with the dihydrocedrene obtained by reducing Cedrene with hydrogen and platinum, nor with the dihydro-iso-Cedrene obtained by Rousset.

A glance at the following table shows the incomplete nature of the evidence in the identification of the various so-called Cedrenes.

Physical constants of "Cedrene" obtained from the natural alcohols:-

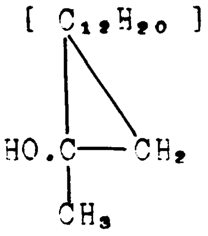
Source	*B.P.*	*Press.*	*d*	*t°*	$n^{15°}$	[α]
Cedrene	124-126°	12mm.	0·9854	15°	1·5028	-60°
Cedrol.	112-113°	17mm.	-	-	-	-
Cedrenol.	117-130°	7mm.	0·981	20°	1·5081 (*)	-3° to +13°
Ψ. Cedrol.	-	-	-	-	-	-

(The figures are Semmler's throughout the table)

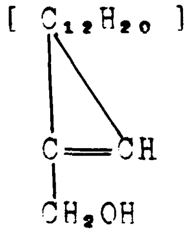
(*No temperature given for this refractive index)

While the work of Semmler and his collaborators shows the close relationship between the natural Cedrene and the hydrocarbons obtained by reduction of the naturally occurring alcohols mentioned on the previous page, it cannot be said to have proved more than that they are probably isomers more or less closely related. That they all yield the same product as one of their oxidation products does not prove them to be identical. Pinene and Bornylene are quite distinct hydrocarbons yet when oxidised with perhydrol Pinene yields Borneol. Again Limonene, Terpinene, and Sabinene are distinct hydrocarbons, and yet they each yield the same product when treated with chromyl chloride, the same product in fact as Cymene gives, viz. p.tolylmethylketone, and from what will appear on a later page it is certain that they all give p.tolylpropaldehyde as well, [Miller and Rohde, Ber., 1890, *23*, 1070-1082; Widman, Ber., 1891, *24*, 439; Miller and Rohde, 1891, *24*, 1356; Henderson Munro and Campbell, J.C.S., 1907, *91*, T.1871; Henderson and Cameron, J.C.S., 1909, *95*, T.969; Henderson, Robertson and Brown, J.C.S., 1922, *121*, T.2717; J.C.S., Robertson, 1924, *125*, 765]. On the other hand Semmler's results would further support the thesis put forward on pp.8-10 that natural Cedrene is not a single hydrocarbon but a mixture of closely related isomers, which by a slight intramolecular change are converted into the same product on oxidation. Whether Semmler's "synthetic" Cedrenes are constituents of the natural Cedrene or merely isomers it is impossible to say.

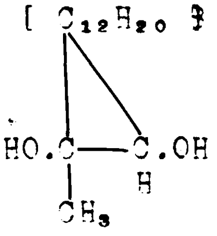
On the assumption that the three alcohols mentioned above are all derived from one hydrocarbon, Semmler has suggested the following formulae:-



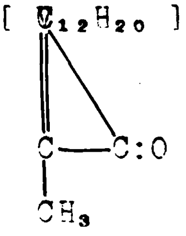
Cedrol.



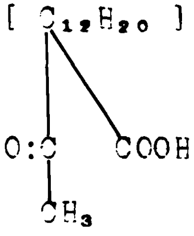
Cedrenol.



Cedrene Glycol.



Cedrone.



Cedrene Keto-Acid.

These formulae are, of course, only tentative, but even on the grounds discussed above there is no need to dispute them as there is still ample room in the rest of the molecule for the explanation of isomers. It is a striking fact that no alcohol has yet been prepared by the oxidation of Cedrene. There is, however, an unpublished result which is of note in this connection. When investigating the action of perhydrol on Cedrene in this laboratory S.T.R.S.Mitchell found that in addition to a small yield of the glycol obtained by Semmler by the action of permanganate on Cedrene, he obtained a considerable yield of a neutral product, b.p., 154-156° / 12mm.; d_4^{20},1·0007 ; n^{20},1·5009 ; $[\alpha]^{20}_{Hg\ green}$ -78·00°;. As it reacted readily with sodium to give a solid derivative it was thought to be an alcohol, but on an analysis there was found C,81·9 H, 11·3 %, agreeing more closely with the oxide $C_{15}H_{24}O$, than with the alcohol $C_{15}H_{26}O$. If an alcohol, it is the first which has actually been prepared from Cedrene. It would be a new alcohol as its constants do not agree with any of the natural alcohols referred to above. The sodium compound reacted with methyl iodide precipitating sodium iodide, with the formation of an oil which was thought to be the methyl ether. It boiled between 140° and 145° /10mm. i.e. 20° above Cedrene and 15° below the alcohol.

Circumstances prevented him continuing this work and the writer took it up at this point. As the yield of the supposed ether was small, dimethyl sulphate was used in place of methyl iodide. Several variations of the method were used. [Tambor, Ber. 1910, *43*, **1882** ; Meldola, J.C.S., 1910, *26*, P.232] Karrer and Lang, Hel. Chem. Act., 1921, *4*, **249**]. The product in each case was distilled under reduced pressure over barium hydroxide. After several distillations two fractions were separated, the lower boiling at 141° / 10mm., the higher and much the larger fraction at 143° / 10 mm. Both fractions were colourless and without characteristic smell. Their constants and analyses were as follows:-

Fraction.	Analyses.	Density.	Refractive Index.
141°/10mm	C= 82·4 % H 11·3 %	$d_{17\cdot4}^{19\cdot5}$ 0.9913	$n_D^{5\cdot5°}$ = 1.5067
143°/10mm	C= 80·70% H= 10·90%	$d_{17\cdot4}^{17\cdot4}$ 0.9959	$n_D^{5\cdot5°}$ = 1.5067 (*)

(*) $n_D^{5\cdot5°}$ for Cedrene = 1.5067

The following table gives the theoretical values for the composition of substances with which the products just described are compared.

Substance.	Formula.	% C.	% H.
Hydrocarbon	$C_{15}H_{24}$	88·14	11·84
Alcohol (Cedrene)	$C_{15}H_{25}.OH$	81·00	11·79
Oxide	$C_{15}H_{24}O$	81·75	10·98
Methyl Ether	$C_{15}H_{25}O.CH_3$	81·28	11·94
Methylated Product	$C_{12}H_{21}O$	80·74	10·[illegible]6
Corresponding Alcohol	$C_{12}H_{18}OH$	80·35	10·71

A comparison of the results with these theoretical values shows that the oxidation product agrees with $C_{15}H_{24}O$ in carbon and with $C_{15}H_{26}O$ in hydrogen. Both are possible products, for it is generally accepted that the action of perhydrol is to give in the first place an oxide which by addition of water gives a glycol: addition of water to the hydrocarbon would give the alcohol.

The analyses of the methylation product, however, do not agree with any C_{15} substance, but they agree closely with the formula $C_{13}H_{21}O$. The analyses of the lower fraction show it to contain carbon and hydrogen considerably in excess even of C_{15}. The only explanation of this is that the lower fraction contains in addition to the substance which constitutes the higher fraction, a hydrocarbon which may either be Cedrene or a new hydrocarbon produced in the process of methylation. The quantity of this fraction did not permit of further fractionation, but it is of interest to note that the mixture of $C_{13}H_{21}O$ and hydrocarbon required by analysis is of the order 4:1. It should be noted that the formation of sodium iodide in the treatment with methyl iodide is no guarantee that the process of methylation has proceeded along orthodox lines. Ewan and Cohen [J.C.S., 1889, 55, T.382] describe an instance in which a ketone was produced by submitting a glycol to methylation. Acenaphthene glycol was treated with sodium and methyl iodide. Sodium iodide was precipitated, but instead of the ether $C_{10}H_6\left\langle\begin{matrix}CH.O.CH_3\\ | \\ CH.O.CH_3\end{matrix}\right.$, a ketone was formed for which they suggest the formula $C_{10}H_6\left\langle\begin{matrix}CH_2\\ | \\ C=O\end{matrix}\right.$. It would appear therefore that in the process part of the Cedrene molecule has been split off giving rise to a product which may not be a methylated compound at all. It is remarkable that the formula of this substance should be of exactly the same dimensions as that obtained by the action of chromyl chloride, (see p.44). There is nothing in the appearance of the two produbts to suggest that thdy are identical, but the coincidence of their formulae would indicate that in the Cedrene structure two of the carbon atoms are combined in such a way as to be peculiarly liable to suffer separation from the molecule. If, on the other hand the product were the ether of an alcohol $C_{12}H_{19}O$ it would recall the acid which Rousset obtained by the oxidation of Cedrene with chromic acid, $C_{12}H_{18}O_3$, [Bull. Soc. Chim.,1897, *17,* (3), 485].

Part I.

(2) The Interpretation of the Action of Chromyl Chloride on the Terpenes.

The Interpretation of the Action of Chromyl Chloride on the Terpenes.

The action of chromyl chloride on substances of the benzene class has been worked out with considerable detail, and the mechanism sufficiently well defined to enable the investigator to predict the products of a new reaction with some degree of certainty. The progress of the reaction when dealing with the much more complicated structure of the terpenes has not yet been, by any means, so thoroughly investigated. As far as these investigations have gone, they have shown that the products obtained on decomposition of the additive compound formed by the action of chromyl chloride on these substances are ketones. aldehydes, and usually chloro-compounds. These may be (1) direct oxidation products of the hydrocarbon, containing the same number of carbon atoms in a molecule of the same configuration: (2) isomers of these in which the positions of the double bonds have been changed or the "bridge" broken: (3) a substance containing fewer carbon atoms in the molecule may be peoduced. As it is obvious that the constitution of the hydrocarbon plays the chief part in determining which of these three types will be produced, it follows that the products of the reaction are of interest, not only from the standpoint of the chemistry of the oxidising agent, but also as pointers in the investigation of the structure of the hydrocarbon, or, at the very least, as confirmation or otherwise of an already postulated structure. With regard to the action of this reagent on the sesquiterpenes the field is absolutely unexplored.

The Mechanism of the Chromyl Chloride Reaction as interpreted by Etard.

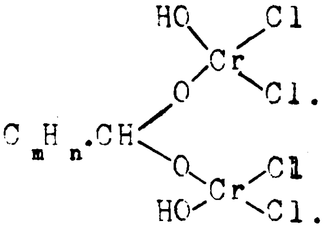
The unfortunate experience of Walter in 1837, which crippled him for life and almost deprived him of sight, apparently scared investigators for more than three decades; for it was not until 1870 that the chemistry of chromyl chloride was re-opened by Carstanjen. In 1877 Haller found that with anthracene he obtained anthraquinone [Comp. Rend., 1877, *84*, 559] It was then that Etard took up the subject and in spite of a few inaccuracies, which will be referred to later, built up a very satisfactory basis for future work. As far as the simple compounds of benzene are concerned his work was thorough and exhaustive; when he arrived at cymene the difficulties were much greater, and his results have been shown to have been inaccurate [Errera, Gazz. 1891, *21*, 76; Miller and Rohde, Ber., 1890, *23*, 1070; 1891, *24*, 1356]. By reason of the analogy of the reagent to chromic acid, Etard expected that it would react both as a chlorinating agent and as an oxidising agent, and was surprised to find that only oxidation took place. His expectations were fully justified when the terpenes were examined.

Beginning with toluene Etard found that the side chain methyl group was attacked, and that he obtained a good yield of benzaldehyde. To protect the methyl hydrogens he introduced a chlorine atom, *i.e.* he used benzyl chloride, and found that the reaction was much retarded; further, that only one molecule of chromyl chloride was added, indicating that one of the methyl hydrogens was actually displaced in the addition. On decomposing the compound, he again obtained benzaldehyde. He then turned his attention to substances which contained one or more substituted groups in the nucleus. These, he found, only retarded the rate of the reaction; the methyl group was attacked in every case. Thus, bromotoluene gave bromo-benzaldehyde, but the para-, meta-, and ortho-, isomers could be separated by the difference in the rates of reaction. The three xylenes gave the corresponding toluic aldehydes, the isomers again reacting in the order already named. In no case did he find that the second methyl group had reacted. Etard, however, does not appear to have tried the reagent on one of the toluic aldehydes: it would seem possible that a compound would be formed $CH_3.C_6H_4.CHO.2CrO_2Cl_2$; for, while the introduction of two molecules of chromyl chloride into the molecule might reasonably be expected to offer sufficient steric hindrance to prevent the introduction of more chromyl chloride, the presence of other groups in the nucleus only retards the reaction, according to Etard's own results. It is therefore probable that a repetition of the treatment would have attacked the second methyl group and given a di-aldehyde.

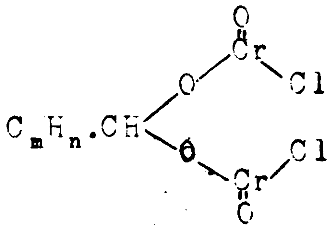
He then concentrated his attention on the benzene nucleus. With benzene, he states, that he obtained quinone, with nitrobenzene nitroquinone, and with nitrotoluene nitrotoluquinone. This last result would appear to be an exception to his general rule that "the methyl group is attacked which is attached to the carbon with most hydrogens", for here the methyl group is not attacked at all. These results were contradicted by Richter [Ber., 1886, *19*, 1060], who repeated the work on nitrotoluene, but obtained, not nitrotoluquinone but nitrobenzoic acid, and again by Carstanjen [J. pr. Chem., 1870, *119*, *(N. F. 2)*, 51], who repeated the work on nitrobenzene and obtained, not nitroquinone but a variety of volatile products which could not be identified. The results of these two investigators were confirmed by Henderson and Campbell, [J.C.S., 1890, *57*, 253], who repeated the reaction many times under different conditions without on any occasion obtaining any quinone. It must therefore be concluded that here Etard was in error, as he was also proved to be in the results of his investigations on cymene, a substance at that time only imperfectly known.

His statement that the additive compound can be readily decomposed with ether with formation of ethyl chloride has been proved by the writer to be quite unfounded. The toluene additive compound was prepared exactly as Etard described, [Ann. chim. phys. [5] 1881, *22*. 218]. It was suspended in dry ether for several days and was found to remain unchanged as long as it was protected from the moisture of the air. It is well known, however, that perfectly dry ether is hygroscopic, and if the suspension has contact with the air, decomposition sets in immediately. There was at no time any suggestion of the vigorous effervescence of ethyl chloride described by Etard. It is possible that the ether which he used contained both alcohol and water, for although he states that the ether was carefully dried, he does not say how this was done.

His explanation of the mechanism of the reaction remains unchallenged. It is as follows. The solid additive compound which separates on the addition of chromyl chloride to a hydrocarbon C_mH_n.has the invariable constitution $C_mH_n.2CrO_2Cl_2$. Since the introduction of one Cl atom into the molecule prevents the introduction of one molecule of chromyl chloride, he suggested the formula (I) for the additive compound of the hydrocarbon $C_mH_n.CH_3$. These compounds give off two molecules of HCl on heating, giving substances of the formula (II).



(I)



(II)

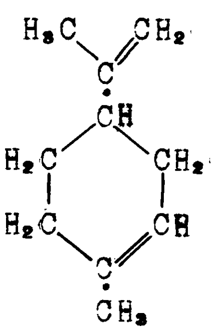
On treatment with water, the conpound breaks up with the formation of $CrCl_3$, H_2CrO_4, and the oxidation product. The third hydrogen is not attacked. He does not attempt to explain the "quinone reaction".

When applied to the terpenes, the reaction appeared to follow very similar lines. Solid additive compounds were obtained of analagous composition $C_{10}H_{16}.2CrO_2Cl_2$, from which two molecules of HCl could be removed by heating. Decomposed by water these compounds yielded ketones, aldehydes, and chlorinated compounds. That the chlorination takes place as the result of the chlorinating power of the reagent has been assumed but not definitely ascertained. It could be due to the addition of HCl during the formation of the additive compound as heat is usually generated and HCl is readily split off from the compound. It might be explained, at least in part, by the almost invariable presence of chlorine dissolved in the reagent. The action of the reagent on ethylenic linkages has not been investigated since Etard's first experiments.

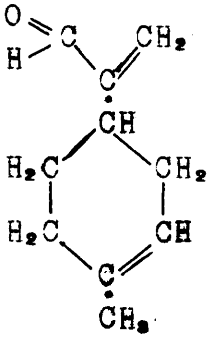
The Interpretation of the Chromyl Chloride Reaction in the Terpene Series.

It has been stated above that the reaction appeared to follow similar lines whether applied to members of the terpene class or to members of the benzene class of hydrocarbons. The products of the reaction, however, would indicate that the similarity was only superficial,,and it must be admitted that Etard's explanation is quite insufficient to account for the products obtained from the terpenes. The writer therefore submits the following thesis.

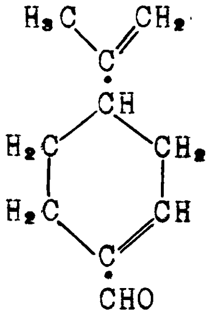
From Etard's conclusions Limonene would be expected to yield at least two aldehydes



Limonene.

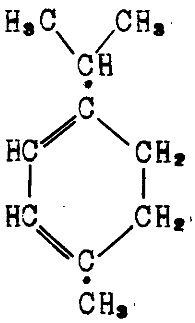


Aldehyde I.

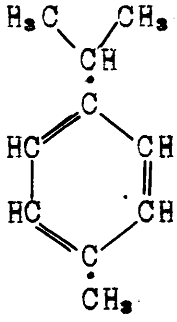


Aldehyde II.

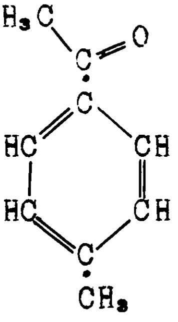
It appeared that one of these aldehydes had actually been obtained [Henderson, Munro, and Campbell, J.C.S., 1907, *91*, T. 1871], together with a ketone $C_9H_{12}O$; but on studying the reaction with terpinene [Henderson and Cameron, 1909, *95*, 969] the resemblance of the products led tp a further examination, which showed that the aldehyde was $C_{10}H_{12}O$, and none other than p.tolyl-propaldehyde; the ketone was likewise found to be .p.tolyl-methyl-ketone. Thus Limonene, Terpinene, and Cymene all gave the same products as under.



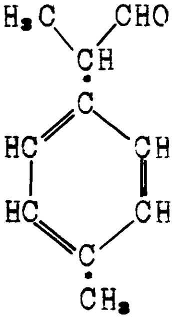
α.Terpinene.



Cymene.

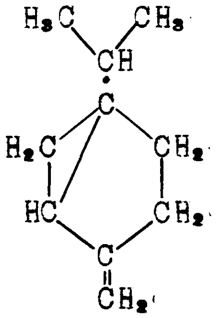


.p.Tolyl-methyl-ketone.

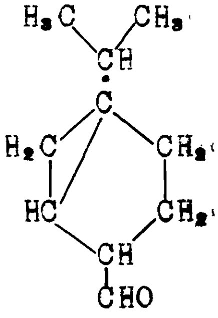


α.p.Tolyl-propaldehyde,

Of the three products from Sabinene none would have been predicted from Etard's rule. In the case of the aldehyde $C_{10}H_{16}O$ not the methyl group but the methylene group was attacked. In the second product the "bridge" was broken and replaced by an ordinary double bond to give an isomer of 4.isopropyl.Δ^3cyclohexanone, while the third was proved to be once more p,Tolyl-methyl-ketone. [Henderson, Brown, and Robeetson, J.C.S., 1922, *121*, T.2717: Robertson, J.C.S., 1924, *125*, 765].

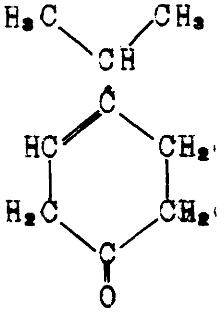


Sabinene.



Aldehyde.

$C_{10}H_{16}O$.



Ketone.

$C_{10}H_{14}O$

The products from the other bicyclic terpenes were as follows:-

Camphene:- Camphenilanaldehyde $C_{10}H_{16}O$, and Camphenilanic acid $C_{10}H_{16}O_2$ [Bredt and Jagilki, Ann., 1900, *310*, 112].

Bornylene:- The same aldehyde as Camphene and a large yield of a chloroketone $C_{10}H_{15}OCl$ [Henderson and Heilbron, J.C.S., 1911, *99*, T.1887].

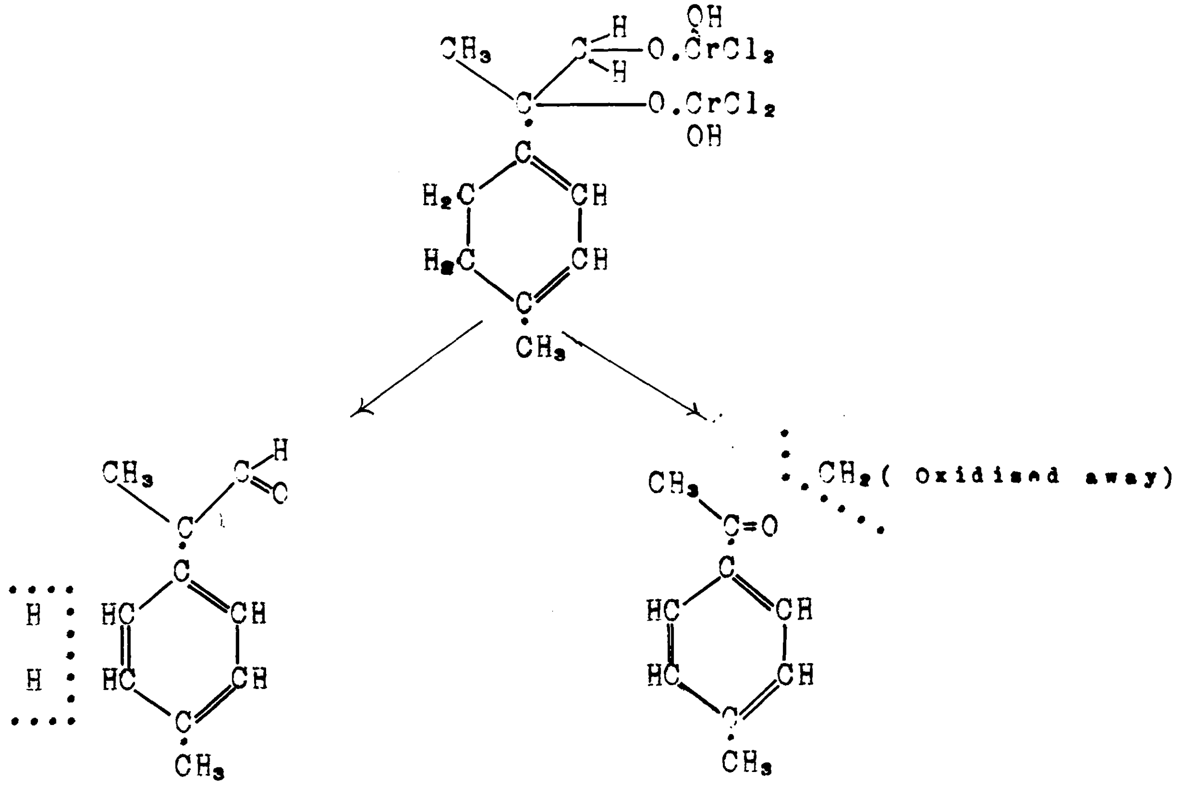
*α.Pinene:-*An aldehyde $C_{10}H_{16}O$ and a ketone $C_{10}H_{16}O$, and a ketone $C_{10}H_{14}O$ or $C_9H_{14}O$, as well as a chloroketonecompound $C_{10}H_{15}OCl$. [Henderson and Smith, J,C.S., 1889, *55,* T.45 : Henderson and Gray J.C.S., 1903, *83,* T.1299 : Henderson and Heilbron, 1908, *93,* T.288].

β.*Pinene:-* a ketone $C_9H_{14}O$, and Pinol glycol, also small amounts of uncharacterised aldehydes and ketones. [Henderson and Chisholm, J.C.S., 1924, *121,* T.2717].

From these results it would appear that the peculiar structure of the terpenes renders the methyl groups less liable to attack than other parts of the molecule, while the persistent appearance of the cymene structure in the products indicates that the stability of its structure has much to do with the direction of the reaction. The rearrangement of the double bonds accompanied in several cases by dehydrogenation,are new features which have not so far been explained in any way whatever, The additive compound alone would appear to be of the same type as in the simpler hydrocarbons, and unless it can be built up on a system of electro- or residual valency, it would appear that Etard's conception of its general structure must stand true; beyond that there would appear to be little similarity.

Considering the case of Limonene first, as a terpene with no "bridge" structure, the formation of p.Tolyl-methyl-ketone and α.p..Tolyl-propaldehyde, show that the reaction has taken place at the double bond, for had the addition taken place at the methylene group with replacement of both hydrogen atoms a ketone and not an aldehyde would have resulted. The products show that neither of the methyl groups has been the point of attack. Further the assumption that the addition takes place at the double bond explains the formation of both the aldehyde and ketone actually found, for the formation of one or other depends on which carbon atom retains the linking oxygen and which parts with it to the chromium again. If "10" carbon atom is oxidised the product will be α.p.Tolyl-propaldehyde; if "8" carbon atom is oxidised the product will be p.Tolyl-methyl-ketone. In assuming that the addition takes place at the double bond, the formation of the additive compound requires two hydrogen atoms which must be supplied from some other part of the molecule. This is precisely what must take place to produce a derivative of cymene. The assumption that the third double bond is produced by the removal of two hydrogens by a process of oxidation is a very natural one indeed. In the formation of α.p.Tolyl-propaldehyde from Limonene it is evident that a more complicated reaction is involved than in the production of benzaldehyde from toluene, for in toto it amounts to this: one of the hydrogens of the ethylene group has been oxidised and a hydrogen atom has been added to "8"..Although it need not be supposed that the same atom which leaves the methylene group attaches itself to the adjacent carbon, it may be said for convenience that this hydrogen atom "wanders", as the process is common to several of the terpenes.

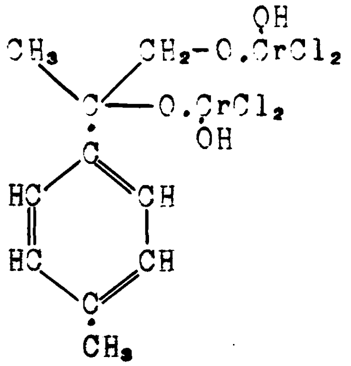
The reaction for Limonene would thus be represented as follows:-



α-p-tolyl propaldehyde.

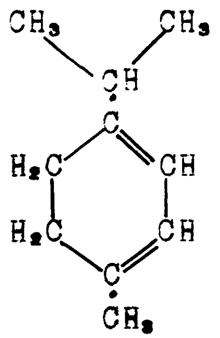
p-tolyl methyl ketone.

The formation of α.p.Tolyl-propaldehyde from cymene could be explained in accordance with Etard's rule, but the simultaneous formation of p.Tolyl-methyl-ketone is left without explanation. If, however, the theory proposed for Limonene is correct the introduction of the second molecule of chromyl chloride should take place at "8" carbon and not at "10" . The additive compound would then be

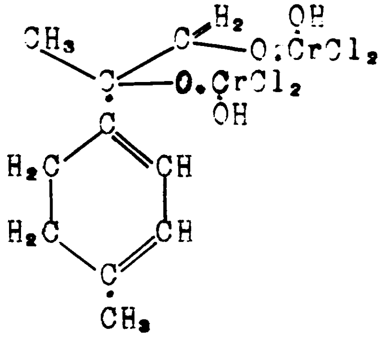


giving, on decomposition, both the products mentioned.

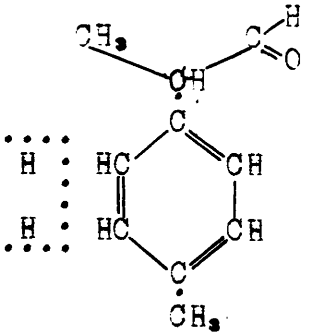
In α.Terpinene the two reactions are, to an extent, combined; the reaction taking place as in the case of cymene, and two adjacent hydrogens being oxidised off as in the case of Limonene to give the third double bond thus:-



α-Terpinene.



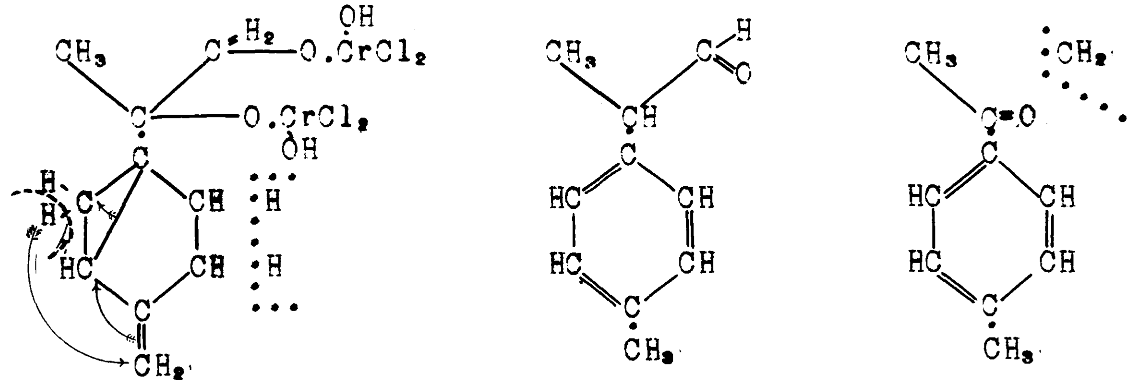
Additive Compound.



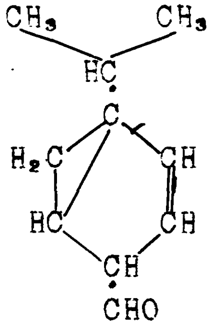
α-p-Tolyl Propaldehyde.

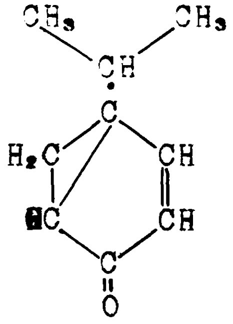
The ketone is, of course, formed as before. *Additive Compound.*

Little can be said with certainty regarding the bicyclic terpenes as the products themselves have at most been descibed only empirically, and frequently much less definitely..With the introduction of the bridge structure differences in the mechanism of the reaction would be expected. This is fully borne out by the results quoted p.29. The formation of α.p.Tolyl-propaldehyde from Sabinene must follow the lines of the cymene reaction, i.e. the addition takes place at "8" and "10" carbons and not at "1" and "7". In the decomposition the directing force would appear to be the stability of the cymene nucleus, and in the removal of the two adjacent atoms of hydrogen it would appear that the stability of the "bridge" is affected, for there results a rearrangement of the double bonds to give the cymene structure, thus:-

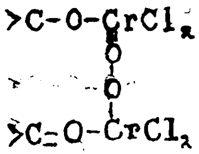


Although not recorded it is highly probable that the accompanying Ketone was also present in the products. The formation of the aldehyde $C_{10}H_{16}O$ would seem impossible on the preceding hypothesis, for its formation implies that addition took place at the double bond since no hydrogen has been removed by oxidation or otherwise, and as the addition at a double bond necessitates the removal of two hydrogens, as explained, the aldehyde expected would be $C_{10}H_{14}O$ with the accompanying ketone $C_9H_{12}O$ shown below



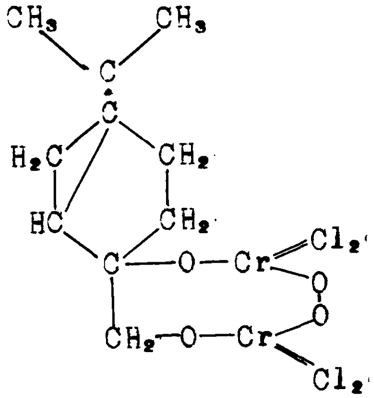


While the number of instances in which the conclusions regarding formulae have had to be revised is proof of the very unusual difficulty in deciding even the empirical formulae of the products with certainty, there is yet another possibility. The uniformity with which chromyl chloride reacts in double molecule suggests that there is a closer connection between the molecules than Etard imagined: the writer therefore makes the further suggestion that Etard's formula only represents a form of the reaction peculiar to the class of hydrocarbons with which he worked, and that the other compound is to be regarded as

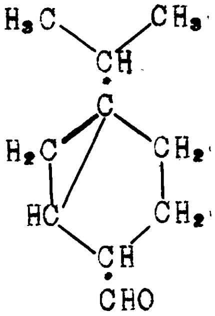


$$\begin{array}{l}>C-O-CrCl_2\\ \qquad\quad\;\; O\\ \qquad\quad\;\; O\\ >C=O-CrCl_2\end{array}$$

The new additive compound for Sabinene now becomes

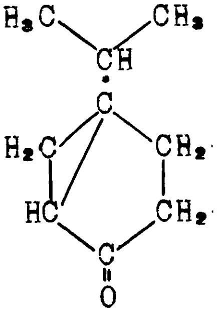


which gives on decomposition with water the aldehyde and ketone



Aldehyde.

$C_{10}H_{16}O$



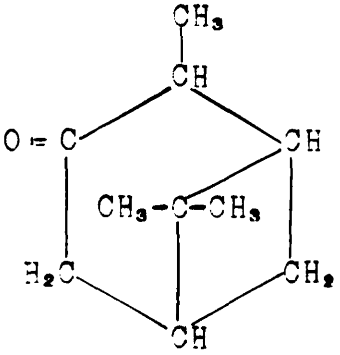
Ketone.

$C_9H_{14}O$

In the same way one would expect the products from Camphene to be the aldehyde $C_{10}H_{16}O$ and the ketone $C_9H_{14}O$ as shown,on p.39.

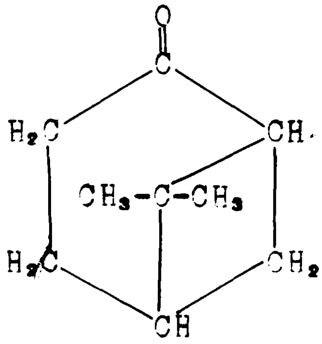
In α.Pinene another new feature is met with. Unlike the two bicyclic terpenes just mentioned, it has no double bond outside the ring. It is therefore doubtful at which point the addition will take place. Of the three methyl groups the one adjacent to the double bond would be expected to offer the least resistence. This is confirmed by the absence of α.p.Tolyl-propaldehyde among the oxidation products recorded; for had either of the other methyl groups been attacked, it is almost certain that the "bridge" would have been ruptured, and as in the previous instances this would undoubtedly have led to the formation of the aldehyde mentioned. If the first mentioned methyl were attacked the previous results would indicate that decomposition of the additive compound would lead to a breaking of the "bridge" and the oxidation of two hydrogens with the ultimate formation of p.isopropyl-benzaldehyde. The aldehyde resulting from the simplest form of the reaction would be $C_{10}H_{14}O$. The formation of the corresponding ketones would involve a complete break in the nucleus. The only aldehyde recorded is $C_{10}H_{16}O$. The formation of this aldehyde demands that both addition and oxidation take place at the double bond, and it would seem impossible to obtain a simple aldehyde in this manner? The products which would be predicted on the suggested hypothesis are shown on p.38 These will be found to agree with the ketone $C_{10}H_{16}O$ actually found and with the revised form of the other ketone also found $C_9H_{14}O$. The third figure p.38 shows the only aldehyde of the group $C_{10}H_{16}$ possible.

The products which would be predicted on the preceding theory from α.Pinene by the addition of CrO_2Cl_2 at the double bond are as follows:-



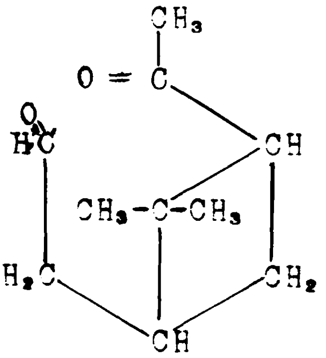
Ketone

$C_{10}H_{16}O$



Ketone

$C_9H_{14}O$

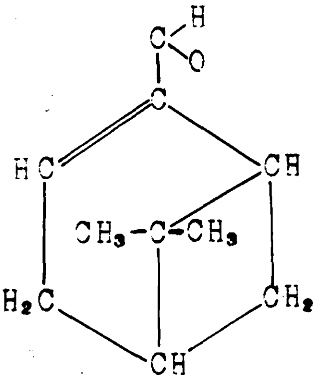


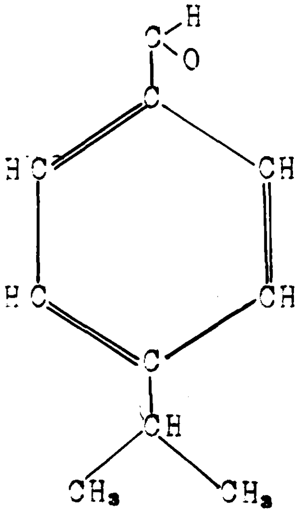
Keto-Aldehyde

$C_{10}H_{16}O_2$

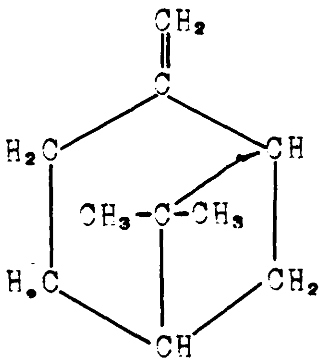
The last compound would not be expected but is shown as the only $C_{10}H_{16}$ possible.

The following represent the products if the methyl group was the point of addition:-



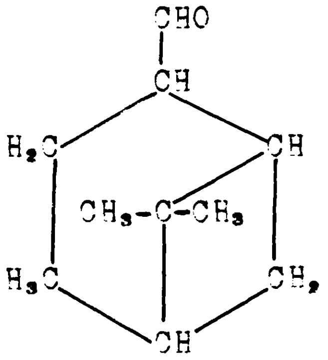


The structure of β.Pinene presents no new feature, but combines those already mentioned. Following the same principle two products would be predicted an aldehyde $C_{10}H_{16}O$ and a ketone $C_9H_{14}O$. Again the hypothesis is justified : The ketone $C_9H_{14}O$ was actually recorded, and a small quantity of an aldehyde which was not characterised. We are therefore now in the the position of being able to suggest the constitution of the ketone with considerable certainty and likewise to suggest both the empirical and structural formula of the aldehyde. They are as follows:-



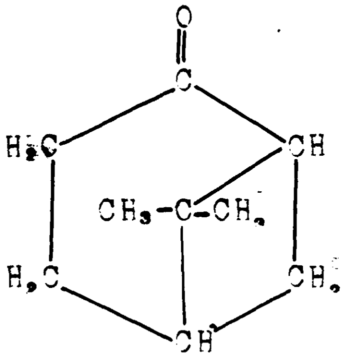
β.Pinene.

$C_{10}H_{16}$



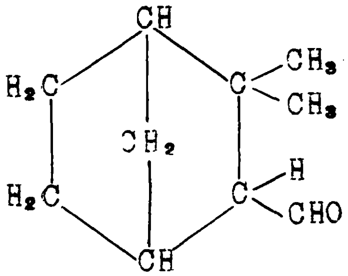
Aldehyde.

$C_{10}H_{16}O$

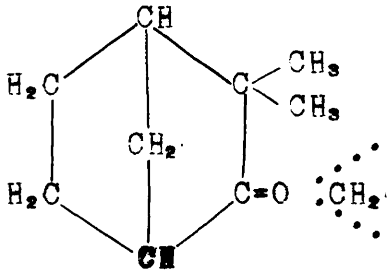


Ketone.

$C_9H_{14}O$



Camphene Aldehyde.



Camphene Ketone.

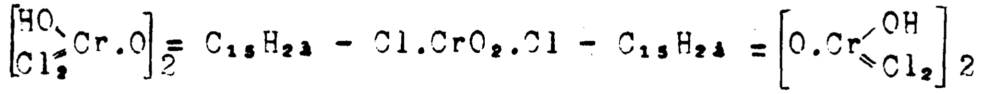
Part I

(3) The Action of Chromyl Chloride on the Sesquiterpene Cedrene,

The Action of Chromyl Chloride on the Sesquiterpene Cedrene.

As with the Terpenes, the action of chromyl chloride on Cedrene is violent and must be moderated by considerable dilution in a suitable solvent. The traditional carbon bisulphide was replaced by carbon tetrachloride, as the latter is more stable towards chromyl chloride and is more easily purified. The reaction seemed to follow orthodox lines and gave a brown additive compound, which behaved in much the same way as those already described. When this compound was analysed, however, it was found that the chromium content varied considerably, and while the results fell between limits which represented 2 and 3 mols. of CrO_2Cl_2 to 1 mol. $C_{15}H_{24}$, it was impossible to decide what addition had taken place. Other investigators in this laboratory experienced the same difficuly with Cadinene and Caryophyllene. J.M.Robertson found the former to unite with something less than 3 mols., while D.T.Gibson found the latter to unite with about 2½ mols. Finally using low temperatures (-5° to -10°) the writer found that Cedrene combined with 2 mols.

This variation recalls Etard's work on xylene, In xylene there were two methyl groups which should have been equally liable to attack and yet only one reacted. In no case yet recorded has a hydrocarbon taken up more than two molecules. This must be due to a lack of space in the molecule. It seemed possible that with the larger sesquiterpene molecule there might be room for another molecule of chromyl chloride. The variations might therefore have been due to the amount of this third molecule which could be forced in at different temperatures. If, on the other hand, the compound were actually $C_{15}H_{24}.2\frac{1}{2}\ CrO_2Cl_2$, it would seem that there was just sufficient room to allow 1 mol. CrO_2Cl_2 to be shared between 2 mols. $C_{15}H_{24}$ If so, the explanation would fall outside the mechanism suggested in the preceding pages. It might be supposed, for example, that the chlorine atoms, with their extra valencies, served as links between the third CrO_2Cl_2 molecule and the two molecules of $C_{15}H_{24}$, giving a compound



$$\left[\begin{matrix}HO\searrow\\Cl_2\nearrow\end{matrix}Cr.O\right]_2 = C_{15}H_{24} - Cl.CrO_2.Cl - C_{15}H_{24} = \left[O.Cr\begin{matrix}\nearrow OH\\ \searrow Cl_2\end{matrix}\right]_2$$

On decomposing such a compound the end molecules of CrO_2Cl_2 would act in the usual way, while those connected through the Cl atoms would be expected to chlorinate the hydrocarbon. While offering a possible solution, this did not appeal to the writer as a probable theory; a more probable explanation was found in other considerations.

In view of the fact that two molecules of HCl can be liberated with comparative ease from the additive compound on the application of moderate heat, it seemed more than likely that the heat of the reaction itself might cause a partial decomposition in small local spaces during the addition of the reagent. If this were so, the solid compound would be a mixture of $C_{15}H_{24}.2CrO_2Cl_2$ and $C_{15}H_{22}.2CrO_2Cl$, in which case an estimation of chromium alone would be misleading in calculating the formula, as the percentage of chromium is now higher. Estimations of Cl varied also, but in the experiment conducted at -5° to -10° it again agreed with 2 CrO_2Cl_2. Until evidence is produced to the contrary the compound must be considered as $C_{15}H_{24}.2CrO_2Cl_2$.

On decomposing the brown additive compound with ice water containing SO_2, to remove H_2CrO_4, a yellow oil was separated containing 3-5% Cl. The oil was freed from resinous matter by distillation in steam, in which it is slightly volatile. The chlorine was removed by prolonged treatment with zinc in alcoholic solution, after which the oil was fractionated. This yielded a clear yellowish oil with a somewhat heavy smell: b.p. 120° / 0·8mm., or 93° / 0·15mm.; $n_D^{15°}$= 1·5462, It gave no compound with sodium bisulphite, but on exhaustive treatment with semicarbazide acetate a solid was obtained which proved to be semicarbazone, although all attempts to crystallise it failed. The whole of the oil was attacked by the semicarbazide as none could be recovered by distillation in steam. It was recovered, however, on decomposing the semicarbazone with oxalic acid. The ketone is probably $C_{15}H_{24}O$. This statement is made with reserve for the following reasons.

Even when the derivatives were crystalline it has proved unwise to state the formula of these products with certainty, for with substances capable of existing in so many isomeric forms the reaction frequently proceeds simultaneously along quite different lines, giving rise to products which are mixtures of substances extremely difficult to separate, and regarding whose constitution the results of analysis alone may lead to quite erroneous conclusions. There is the further difficulty that even if only a small amount of impurity is present the difference in the percentage of carbon caused by the removal of a methylene group, for example, is not more and possibly less than that caused by the presence of an impurity. The same set of circumstances arose in this work as was encountered in the simpler terpenes during the study of the action of chromyl chloride on pinene (Henderson and Gray etc, J.C.S., 1903, *83*, T.1299 : 1908, *93*, T.288). Here the authors obtained an oil, the analysis of which proved it to be a ketone $C_{10}H_{14}O$. Later work, however, argued that its formula was $C_9H_{14}O$, the difference being caused by impurities, yet it gave a crystalline semicarbazone, which even after careful purification gave a value for nitrogen 1 % below the theoretical value. Other instances of a similar nature have been mentioned in these pages.

The evidence for the formula stated on the previous page is as follows. The completeness of the semicarbazide reaction, the recovery of the ketone, and the nitrogen content of the solid derivative, show that this consists of a semicarbazone or semicarbazones. The carbon and hydrogen analyses indicate that it is the semicarbazone of the ketone $C_{15}H_{24}O$: $C_{16}H_{27}N_3O$ requires

C, 69·26; H, 9·82; N, 15·15:

The results found were

C, 70·73; H, 9·82; N, 14·49: (1st. prep^{n}.)

C, 70·46; H, 10·65; N, 14·49: (purified)

The analyses of the ketone itself agree closely with $C_{13}H_{21}O$, which requires

C, 80·74; H, 10·96:

The results found were

C, 80·97; H, 10·60:

The ketone $C_{15}H_{24}O$ requires

C, 81·75; H, 10·99.

As the oil could only be purified by a very limited fractionation at a low pressure, the agreement with the formula $C_{13}H_{21}O$ must be waved in favour of the other , as the analyses of the semicarbazone do not admit of its consideration: $C_{14}H_{24}N_3O$ would require

C, 67·16; H, 9·67; N, 16·79.

The determination of the molecular weight, 224, also confirmed the formula $C_{15}H_{24}O$ which requires 220.

While this conclusion is the only one which the results will allow, the strange agreement between the formula from the analysis of this ketone and that obtained on submitting the product from the oxidation with perhydrol to methylation would suggest something more than coincidence. Much more work will be necessary before anything more definite can be stated.

An attempt to prepare a crystalline semioxamazone, kindly undertaken by Prof. F.J.Wilson, did not prove successful.

The oil reacted with sodium to give a red solid, which was decomposed by water, from which an oil was reprecipitated on addition of a mineral acid.

It did not react with dilute nitric acid, but was decomposed by 30% acid giving a resinous product.

The chloro=compound was not isolated.

Part I.

Experimental.

EXPERIMENTAL.

Preparation and Examination of the Hydrocarbon.

To prepare pure Cedrene Rousset recommended that it be distilled over sodium. In the experience of the writer, this should be used, if at all, with caution, as it causes considerable resinification, and the formation of dihydrocedrene which boils at a temperature just below Cedrene, is more likely to cause trouble than the naturally occurring alcohols which boil sufficiently above Cedrene to allow of their separation by ordinary fractionation.

Distillation was carried out under reduced pressure by means of a Geissler pump, the pressure being measured by a simple column of mercury open to the air. A manometer was used in the first experiments, but owing to the difficulty of excluding all trace of air from the closed limb, this was abandoned. A series of observations were made to observe the boiling points under still lower pressures, using a mercury pump reinforced by a water pump. These observations showed that varying conditions had too great an effect on the boiling point for such low pressures to be used for purposes of separation or comparison. The readings made at 1 mm. are shown on p.47 .

These figures show that a given temperature and pressure are alone insufficient data to fix a fraction, at low pressures.

The reason for this is that quite a considerable amount of distillate could be collected although the liquid in the flask was not boiling, but evaporating without ebullition. The result is, that what at ordinary pressures would cause a difference in boiling point of about ½°, at low pressures causes a difference of 5° to10°. Such a rise and fall was obtained by doubling the rate of distillation and reducing it by half. The fall of the thermometer in the middle of the observations shows that the rise in temperature was not due to the presence of a higher boiling fraction.

Readings with Temperature Rising			Readings with Temperature Falling		
Rate of Distillation in Drops per Min.	Boiling Point	Bath Temp.	Rate of Distillation. in Drops per Min.	Boiling Point	Bath Temp.
27.3	78°	120°	12.0	73°	116°
26.9	77°	118°	15.7	74°	120°
26.9	77°	116°	33.3	78°	130°
25.0	76°	115°	31.5	79°	180°
21.4	76°	114°	40.0	81°	134°
20.0	75°	112°	40.0	81°	140°
18.2	74.5°	110°	40.0	83°	140°
17.6	74°	109°			
8.0	73°	104°			

100 cc. of Cedrene, supplied by Messrs W.J.Bush and C^{o}, were refluxed with sodium for one hour and distilled under

reduced pressure; the fraction boiling 120°-130° was redistilled and the constants of the following fractions observed. (1) 120°, (2) 121°, (3) 122°, (4) 123°-125°, (5) 125°-130°. all at 12mm. All the fractions were of about the same volume, with the exception of (5) which was about half the others.

Optical Rotation:- (Observed at 13.5° ; light supplied from bunsen flame with sodium salt; observations made in 5 cm. tube verified for sign in 10cm.)

Fraction	Readings.			$[\alpha]_D^{13.5°}$
	Zero	180.92°	0.88°	
120°	Av.	149.84° -31.08°	329.87° -31.01°	-62.1°
121°	Av.	149.65° -31.27°	329.48° -31.40°	-62.67°
122°	Av.	152.26° -28.66°	332.30° -28.58°	-57.24°
123-125°	Av.	153.65° -27.27°	333.65° -27.23°	-54.50°
125-130°	Av.	161.08° -19.85°	341.14° -19.77°	-39.62°

Refractive Index:- (Observed at 13.5°; light supplied from bunsen flame with sodium salt; at 13°, using Pulfrich Refractometer prism u = -1.62)

Fraction	Reading.	$n^{13.5^\circ C}_D$	$n^{15^\circ}_D$ (Corrected using the following table)
120°	37°48.5'	1.50359	1.50289
121°	37°42.5'	1.50369	1.50299
122°	37°37.0'	1.50421	1.50351
123°-125°	37°14.0'	1.50685	1.50565
125°-130°	36°55.9'	1.50808	1.50733

While the specific refractivity is a constant for all temperatures the refractive index varies considerably, As it seldom happens that two experimenters record their results at the same temperature, the observations are of little use for comparison purposes. The following observations were made with a view to obtaining the corrections necessary to bring readings made at different temperatures to a common basis; (see p.50.).

As the pressure obtainable at any time depends on the prevailing atmospheric conditions, boiling points are seldom recorded at the same pressure. The following observations were made, ~~that~~ that the data of other workers might be brought to a common basis, and hence of value for comparison.

Differences in refractive index due to differences in temperature.

Fraction	Ref^{n} Angle.	Angle Diff	Temp^{re}.	Diff.	Angle Diff/1°	Index Diff/1°
120°	38° 8.5'	17.5'	18.5°	3.5°	5'	.00047
	37°51.0'		15.0°			
121°	38°13.5'	6'	20.5°	1.5°	4'	.00038
	38° 7.5'	4.5'	19.0°	1.0°	4.5'	.00043
	38° 3.0'	3'	18.0°	1.0°	3'	.00028
	38° 0.0'	5'	17.0°	1.0°	5'	.00047
	37°55.0'	5'	16.0°	1.0°	5'	.00047
	37°50.0'		15.0°			
123°	38° 0.0'	15'	18.0°	3.0°	5'	.00047
	37°45.0'		15.0°			

Average decrease in Refractive Index per 1° rise of temperature = .00043 .

The Changes in Boiling Point caused by Changes in Pressure.

(The values refer to the 121° fraction)

Temp. °C.	Press. mm.	Temp. °C.	Press. mm.	Temp. °C.	Press. mm.
133	19	124	12	126	13.5
132.5	17.5	127	14	125	13
131	17	129	15.5	124	12.5
130	16	128	15	124	12
128	15	127	14	123	11.5(*)

(*) boiling point beginning to rise

For convenience, these values have been plotted, the graph being shown on p.4.. A consideration of the values shows that as the pressure rises the difference in boiling point per 1mm. change decreases, as would be expected: between 11mm. and 14mm there is a fall of about 2° / 1mm; at 17mm the fall is only about 1° / 1mm.

About 600 cc. of Cedrene (W.J.Bush and C^{o}.) were distilled without treatment with sodium and separated into the fractions as shown below, along with their physical constants.

Fraction	Density	Refractive Index	Dispersion $\mu_F-\mu_C$	Mol. Refr.	Rotation $[\alpha]^{19.5°}_{Hg}$
128°-129.5°	$d^{23.7°}_{15°}$=0.9305	$n_D^{25.8°}$=1.4975	.01009	64.81	-63.81°
129°-131°	$d^{23.5°}_{15°}$=0.9822	$n_D^{25.8°}$=1.4995	.01151	64.45	-60.34°
134°-136°	$d^{24°}_{15°}$=0.9869	$n_D^{25.6°}$=1.5036	.01159	64.54	-30.32°
136°-140°	$d^{24.2°}_{15°}$=0.9406	$n_D^{25.5°}$=1.5048	.01192	64.43	
140°-150°	$d^{24.2°}_{15°}$=0.9546	$n_D^{25.3°}$=1.5071	.01207	63.72	+ 3.78°
150°-160°	$d^{24°}_{15°}$=0.9842	$n_D^{25.3°}$=1.5096	.01275	62.05	+ 9.88°

The densities and refractive indices were observed later at 15° and recorded for comparison. The refactive indices were corrected from the table p.50; the results are tabulated alongside in the table on the following page.

Fraction B.P. 17mm.	Density $d^{15°}_{15°}$	Refractive Index. $n^{15°}_{D}$	
		.Corrected from table p.[illegible] to 15°	Observed at 15°
128°-129.5°	0.9362.	1.5021	1.5024
129°-131°	0.9391.	1.5042	1.5043
134°-136°	0.9439.	1.5081	1.50[illegible]
140°-150°	0.9618.	1.5116	1.5119
150°-160°		1.5141	1.5140

From the first sample of Cedrene, the fraction boiling at 121° / 10mm. and feom the second the fraction boiling at 129-131° / 17mm. were used for the oxidation experiments.

The Action of Chromyl Chloride on Cedrene.

In preparing the reagent the original method of Thorpe [J.C.S., 1878, *21*, 514] was at first employed : later on the more economical method of Moissan [J.C.S., 1884, *46*, 1267] using HCl and CrO_3 was adopted. Finally the reagent was obtained from Messrs Boots and C°, Ltd.

The Preparation of the Additive Compound and its Constitution.

Following the example of Etard, other workers have used carbon disulphide as solvent and diluant: it has the advantage that its low boiling point prevents excessive rise of temperature if ordinary care be observed. On the other hand it has the disadvantages of particularly high inflammability, an obnoxious smell, and poisonous nature which is accentuated by the formation of the very poisonous phosgene gas as a result of the action of chromyl chloride on it. For these reasons carbon tetrachloride was used in its place, for chromyl chloride has practically no action on it; it is non-inflammable although also highly poisonous. It is easily purified and is altogether a much more convenient solvent.

The reaction between chromyl chloride and Cedrene is violent. Even when the reacting substances are diluted, there is a perceptible crack when the two meet unless the dilution is very great. The following dilutions were used: 90 cc. Cedrene, 129°-131° / 17mm. (122°-123° / 12mm) were diluted to 1000 cc., 200 gms. CrO_2Cl_2 were likewise diluted to 1000 cc., and these were added alternately in small quantities to another 1000 cc, of the solvent, CCl_4. No external cooling appeared necessary, as with this dilution there was no great tendency to heat up. To ascertain when the reaction was complete, a sample of the solution was filtered rapidly at the pump, after standing for some time to allow the action to complete itself; an excess of chromyl chloride was shown by the reddish colour of the filtrate. An estimation of the chromium in the filtrate on one occasion showed it to contain 3·468 gms. CrO_2Cl_2 per litre. When half the reacting substances had been added, the mixture was allowed to stand for 2-3 days and the brown additive compound filtered off and washed with CCl_4. The filtrate was then used for the second portion. No attempt was made to abstract the last traces of solvent from the precipitate as the compound readily decomposes in contact with air. When required dry for analysis , this was done in a vacuum desiccator over sulphuric acid. It was found advisable to "dry" the sludge in all cases, as the powder could be decomposed more efficiently.

In all the reactions hitherto reported in which chromyl chloride attacked a hydrocarbon, the additive compound has been found to contain 2 CrO_2Cl_2 united to 1 mol of hydrocarbon. It was therefore considered sufficient to estimate the chromium content of the compound obtained. This was done as follows:- A weighed quantity of the additive compound was placed in a nickel crucible and decomposed by gentle heating. When all the HCl had been driven off the temperature was gradually raised. This had to be done with care owing to the danger of sudden deflagration. After burning off the carbon the residue was mixed with sodium peroxide and fused, dissolved in water, filtered to remove nickel, the filtrate acidified, and hydrogen peroxide decomposed by boiling. The chromate was reduced by a known volume of standard ferrous ammonium sulphate, the excess being titrated with dichromate.

Wt. of Compound.	%Cr.
0.7468 gms.	21.55
0.2902 gms.	21.18
0.1824 gms.	22.41
0.1578 gms.	23.47

The differences between these results showed the presence of something unexpected. They indicated that there had been an addition of 2-3 mols. of CrO_2Cl_2 to 1 mol. of hydrocarbon. The similar experiences of other workers have been mentioned on p.40.

These estimations had been made on the assumption that the compound was one of simple addition. If, however, for any reason the compound lost 1 mol. of HCl , the solid would become a mixture of substances with varying analyses according to the conditions of experiment. It was therefore apparent that this part of the work was no longer one of confirmation but one of investigation. Estimations of chlorine in two different samples at hand gave the following results

Wt. of compound.	Wt of AgCl.	% Cl.
0.1462 gms.	0.1626 gm.	27.5
0.2697 gm.	0.1968 gm.	18.2

If these figufes are compared with the tables below it will be seen that although those for Cr fall between 2and 3 mols. CrO_2Cl_2, they also fall between 2 mols. CrO_2Cl_2 and 2 mols. CrO_2Cl, and that the values for Cl also fall between the last two values. There was certainly a suggestion of HCl fumes during the reaction, but as the presence of CrO_2Cl_2 fumes would account for this, it signified nothing.

Theoretical Values for various Additive Compounds.

	$C_{15}H_{24}.CrO_2Cl_2$	$C_{15}H_{24}.2CrO_2Cl_2$	$C_{15}H_{24}.3CrO_2Cl_2$
% Cr	14·54	20·22	23·32
% Cl	19·81	27·57	31·78

	$C_{15}H_{22}.2CrO_2Cl$	$\left\{\begin{matrix} C_{15}H_{24}.2CrO_2Cl_2 \\ C_{15}H_{22}.2CrO_2Cl \end{matrix}\right.$	$\left\{\begin{matrix} C_{15}H_{24}.2CrO_2Cl_2 \\ 2[C_{15}H_{22}.2CrO_2Cl] \end{matrix}\right.$
%Cr	23·58	21·78	22·36
%Cl	16·17	22·30	20·34

The significance of these figures, as dealt with elsewhere in this thesis, led to a reinvestigation of the matter, the directing principle now being to prevent the loss of HCl during the reaction. With this in view, the process was repeated, but with even greater care than before at a temperature of -5° to -10°.

45 cc. (42 gms.) Cedrene b.p. 129°-131° / 17mm. were dissolved in 500 cc. CCl_4, 100 gms. CrO_2Cl_2 were dissolved in 1000 cc. of CCl_4 and cooled to -5°. Small quantities of the Cedrene solution were now added to 1500 cc. of the solvent cooled to -10°. The cooled CrO_2Cl_2 was run in alternately through a very fine dropping nozzle. The flask being kept all the time in a freezing mixture. The reaction occupied from 4 to 5 hours. When complete the mixture was allowed to stand in a well stoppered flask for 2 days. The solution remained dark red with the excess of CrO_2Cl_2. The additive-compound was filtered off at the pump, washed with fresh solvent, and removed at once to a vacuum desiccator, where the remainder of the solvent was removed over sulphuric acid. The last traces of solvent are removed with difficulty and from 10 to 14 days are required for this part of the work. After about 3 days drying the lumps require breaking up. Advantage was taken of this to prepare a sample for analysis. The outside of the lumps being slightly decomposed

were removed and only the inside portions kept for analysis. The chromium in this case was estimated as Cr_2O_3 on ignition of the compound, and subsequent treatment with nitric acid followed by re-ignition. The following are the results.

Wt. of Compound.	wt. of Cr_2O_3	% Cr.
0.3286 gm.	0.0959 gm.	20.02
0.5570 "	0.1650 "	20.04
0.4924 "	0.1462 "	20.08

Direct estimations of chlorine in the additive compound gave results which were variable but always higher than the possible value. On the other hand, estimations of Cl made after decomposition of the compound were always lower than the value required to satisfy the chromium content.

After all the amount of the reagent actually absorbed in the reaction is sufficient proof of the general constitution of the additive compound. This was found to agree almost exactly with the amount required to give $C_{15}H_{24}.2CrO_2Cl_2$.

10gms. Cedfene absorbed 15·4g. CrO_2Cl_2 leaving 3·0 g. in the solvent. 10gms. $C_{15}H_{24}$ require 15·2 g. to give $C_{15}H_{24}.2CrO_2Cl_2$.

Decomposition of the Additive Compound, and Examination of the Oxidation Product.

The sludge, consisting of additive compound and solvent, can be decomposed directly, but owing to the formation of clots (by reason of the immiscible nature of CCl_4 and water), with the consequent uneven distribution of the compound, it was found inadvisable on account of the local heating which resulted. The compound was therefore "dried" in a vacuum desiccator over sulphuric acid until it could be powdered; it was then added gradually to a large bulk of ice-water, through which a current of sulphur dioxide was passed at such a rate as to maintain a slight smell of the gas. By this means chromic acid was reduced as fast as it was formed. After standing for 2 days the oxidation product was extracted with ether. Chloroform, petroleum ether and carbon tetrachloride were also used but no advantage was obtained.

On removing the ether a viscous, yellow oil was obtained which was distilled in steam, yielding a clear yellow oil, and leaving a thick tarry residue containing some chromium. The oil, however, distils very slowly in steam, so slowly, in fact, that even when salt is added to raise the boiling point and the distilling flask kept at boiling point in an oil bath, the distillation required about 24 hours. This naturally entails a considerable loss, as much of the product resinifies in the process. Distillation at a pressure of 1-2 mm. did not prove any more satisfactory. The oil had a heavy smell suggestive of an aldehyde or ketone, but treatment with sodium bisulphite gave no crystalline compound. All attempts to induce the oil to crystallise failed. An analysis of the oil gave the following results:-

Wt of Oil ___________0.2054 gm

Wt of H_2O ___________0.1829 " = 75.90% C

Wt. of CO_2 ___________0.5716 " = 14.14% H.

An estimation of the product from one oxidation gave

Wt. of Oil___________0.3441 gm.

Wt. of AgCl___________0.0873 " = 3.56% Cl.

An estimation of the product from another oxidation gave

Wt. of Oil(126-145°/ 1mm.) 0.4500 gm.

Wt. of AgCl_________________0.0572 " = 4.18% Cl.

Attempts to make a semicarbazone at this stage were quite unsuccessful.

An effort was now made to remove the chlorine from the compound in the hope that a product would be obtained from which a pure product could be distilled. If HCl had been added at the double bond a derivative of dihydro-cedrene would be expected from the chlorinated portion. The oil was treated with zinc dust in alcoholic solution for 6 - 8 weeks. During this period the solid (zinc and zinc chloride) was filtered off from time to time, fresh zinc added to the alcoholic solution , and the solid estimated for chlorine. Calculated on 100 gms. oxidation product the extraction proceeded as follows:-

After treatment	with zinc for		1 day	extracted	.7gm.Cl
"	"	a further	4 days	"	1.4 "
"	"	"	6 "	"	1.7 "
"	"	"	14 " (*)	"	.8 "
"	"	"	7 weeks	"	.1 "
					4.2gm.Cl.

[(*) allowed to stand over vacation]

An estimation of chlorine in the oil recovered from the above treatment gave the following:-

Wt. of Oil ____0.3896 gm.

Wt. of AgCl____0.0093 gm. = 0.59%Cl.

The oil from the zinc-alcohol treatment was distilled under reduced pressure, the largest fraction distilling about 120° / 0.8 mm.. It was a clear, pale yellow oil.

Pressure of other work interrupted this work, and when it was resumed the oil had darkened a little. For the purpose of removing any resinous acid which might have been produced in the interval, the oil was treated with a dilute solution of potash in methyl alcohol. This treatment caused considerable resinification. The purified oil was distilled in steam and then in vacuo. After several distillations the main fraction boiled at 93° / 0·15 mm., $n_D^{15°}$ = 1·5462. The results of analysis were as follows:-

(1)

Wt. of oil_____0.2596 gm.

Wt. of H_2O______0.2472 gm. ______ = 10.65% H

Wt. of CO_2______0.7704 gm. ______ = 80.93% C.

(2)

Wt. of oil ____0.2449 gm.

Wt. of H_2O ____0.2818 gm. ______ = 10.56% H.

Wt. of CO_2 ____0.7276 gm. ______ = 81.02% C.

Mean of Results___ H = 10·60 %
C = 80·97 %.

Preparation of Semicarbazone.

2 to 5 gms. of the oil were added to an alcoholic solution of semicarbazide acetate (2 mols.) prepared as follows:- semicarbazide hydrochloride was dissolved in the minimum of water, and to it added an alcoholic solution of potassium acetate in slight excess. The potassium chloride which separated, was filtered off and the filtrate used for

for preparing the semicarbazone. As repeated attempts failed to give any evidence of a crystalline product, the solution was allowed to stand for 3 to 4 weeks. During this time a solid separated out. Alcohol was renewed as it evaporated. The solid was filtered off and thoroughly treated with alcohol in which it was insoluble. It crystallised from hot water in flakes and in cubes, according to conditions, m.p. 260°. Analysis gave

Wt. of solid ....l. .0.0418 gm.

Vol. of nitrogen at 15.5°, 751.7 mm. = 17.5 cc.

= 49.55 % N.

This solid is a product of polymerisation of semicarbazide.

All efforts to obtain a crystalline substance from the alcoholic solution failed. The oil which it contained was distilled in steam but yielded no distillate. As the original oil was distillable in steam, it follows that it has undergone some complete change. The residue in the distilling flask, although oily during the distillation solidified to a yellow mass when cold. It was very readily soluble in all solvents except water. As before, all attempts to crystallise it failed. An estimation showed that the crude material contained 13 % N. This was strongly suggestive of a semicarbazone, and as crystallisation had failed it was purified by projecting the alcoholic solution into distilled water with constant agitation. By this method the compound was precipitated as a white flaky powder; any resin coagulated at the surface as a sticky layer and adhered to the sides of the vessel; any semicarbazide remained in solution. The process was repeated until no resinous scum separated. Obtained in this way the compound was a white amorphous solid which could be dried in a vacuum desiccator. If placed in a steam oven it melted at a temperature below 100° to a clear mobile liquid, but at 100° it soon began to darken in colour. On cooling it set to a hard vitreous solid.

As semicarbazones may combine with alcohol, which can be removed at 100° [J.C.S., 1909, *95*, T.969], a weighed quantity was dried at 100° for 2 hours.

Wt. of compound.......0.1646 gm.

Wt. after drying for 2 hours at 100° ....0.1621 gm.

Loss in wt. 0.0025 gm. ...= 1.8 %

The loss might be entirely explained by the decomposition which took place during heating.

Analyses gave the following results:-

(1) 1st. Preparation.

Wt. of compound.......0.1866 gm.

Vol. of nitrogen at 21°, 748.9 mm. .17.3 cc.

= 14.49 % N.

(2) Purified.
Wt. of compound...... 0.3181 gm.

Vol; of nitrogen at 22° , 764.15 mm.= 39.5 cc.

= 14.40%.

(3) 1st. Preparation
Wt. of compound ..... 0.1914 gm.

Wt. of H_2O............ 0.1680 gm. .... = 9.82 % H

Wt. of CO_2 ....0.4948 gm. .... =70.73 % C

(4) Purified.

Wt. of compound.......0.0772 gm.

Wt of H_2O ....0.0735 gm................. = 10.65 %H

Wt. of CO_2..............0.1994 gm. .... = 70.46 %C

Mean results C, 70·59 %, H, 10·23 %, N, 14·44 %.

The solid was decomposed with oxalic acid, and distilled in steam. It yielded an oil which on analysis gave the following results

Wt. of oil ....0.1602 gm.

Wt. of H_2O ....0.1557 gm. .... = 10.87% H.

Wt. of CO_2 ....0.4695 gm. .... ==79.95% C.

With hydroxylamine an oil was obtained which boiled 140°-150° 0·2 mm.

Dilute nitric acid had no reaction on the oxidation product. 80 % acid gave a product , which after treatment with ammonia, gave a flocculent silver salt..Analysis showed this to be the salt of a resin acid..

The action of bromine is somewhat similar to its action on Cedrene. There is evidence of unsaturation but the reaction slows down to such an extent that it is impossible to judge the end point. The retardation begins after the first cc. has been added. (about 30 cc. being required for one unsaturation) .

The molecular weight of the oxidation product was found.

(1)
Wt. of benzene ......22.95 gm.
Wt. of compound ..... 0.1564 gm.
Depression in freezing point = 0.155°.

(2)
Wt. of benzene .....22.66 gm.
Wt. of compound .... 0.2868 gm.
Depression in freezing point ... 0.290°.

In calculating the molecular weight from the formula $M = \frac{k \times w}{d \times W}$ the value of k must be determinrd for a suitable substance. The most suitable substance in this case was Cedrene.

Wt. of benzene	31.41 gm.	31.28 gm.
Wt. of Cedrene	.1438 gm.	.3564 gm.
Lowering of freezing point	0.115°	0.285°
	k = 5129	k = 5107

Using the mean value for k, 5118, the values for the molecular weight are:

$M = 225$, and $M = 223{\cdot}5$.

A micro estimation in camphor by J.Woodburn in this laboratory gave the value 223.

There is therefore no doubt that the substance has a formula of the order $C_{15}H_{24}O$.

Part I.

(4) The Action of other Reagents on Cedrene.

Investigation of a Product obtained in the Oxidation of Cedrene with Perhydrol.

Oxidation of Cedrene with perhydrol gave, in addition to a small yield of glycol, a neutral product (see p, 17) . Methylation of this product with dimethyl sulphate was carried out as follows: [Tambor, Ber.,1910, *43*, 1882 ; Meldola, J.C.S., 1910, *26* , P.232 ; Karrer and Lang, Hel. Chem. Act., 1921, *4* , 249] .

(1) 5 gms. of the neutral product were dissolved in 35 gms. of benzene and refluxed with sodium until the reaction was complete. Excess of dimethyl sulphate was added along with sodium bicarbonate (to neutralise any sulphuric acid formed in the course of the reaction). When the reaction was complete the excess of dimethyl sulphate was driven off, the product extracted with ether, dried and distilled in vacuo over $Ba(OH)_2$ This last is necessary as a little dimethyl sulphate remains in the product , and decomposing as distillation proceeds gives rise to free sulphuric acid. By reason of this the product first becomes dark purple and finally chars completely. With the alkali present there is not even darkening in colour. Distillation gave an oil b.p. 120°-150° / 10mm. After several distillations over $Ba(OH)_2$ two distinct fractions were separated, boiling at 141° /10mm. and 143°/10mm. respectively.

(2) 10 gms. of the neutral product were dissolved in methyl alcohol containing 50 gms. sodium hydroxide. To this was added 20 gms. dimethyl sulphate : a trap of alkali was used to prevent the poisonous dimethyl sulphate escaping into the air. When the reaction had subsided the temperature of the bath was raised to about 60°. More dimethyl sulphate and alkali were added occasionally, and the whole finally heated for several days on an almost boiling water bath to ensure the decomposition of the excess of dimethyl sulphate. Water was added and the oil extracted with ether and distilled as above. This method gave a good yield.

Analyses.

141° Fraction.

(i)
Wt. of Oil 0.2125 gm.
Wt. of H_2O 0.2171 gm. ______________= 11.43 % H
Wt. of CO_2 0.6443 gm. ______________= 82.69 % C

(ii)
Wt. of Oil 0.2213 gm.
Wt. of H_2O 0.2231 gm. ______________= 11.28 % H
Wt. of CO_2 0.6670 gm. ______________= 82.20 % C

Mean Results H = 11·3 %
C = 82·4 %

143° fraction.

(1)

Wt. of Oil 0.2259 gm.

Wt. of H_2O 0.2198 gm. ________________ 10.89 % H

Wt. of CO_2 0.6674 gm. ________________ 80.57 % C.

(2)

Wt. of Oil 0.2246 gm.

Wt, of H_2O 0.2193 gm. ________________ 10.92 % H

Wt. of CO_2 0.6659 gm. %________________ 80.83 % C.

Mean Results H = 10·90 %.
C = 80·70 %.

Action of Sulphuric Acid on Cedrene.

Following Bertram's method (Wallach, Ann., 1892, *271*, 288) 20 gms. Cedrene b.p. 120° / 10 mm, $n_D^{15^\circ}$ 1.5923 ; $[\alpha]_D^{13{\cdot}5^\circ}$ -62.1°. were dissolved in 800 gms. of glacial acetic acid to which were added 16 gms. H_2SO_4 in 32 gms. H_2O. This mixture was heated on a water bath for three days with reflux condenser. On the addition of the sulphuric acid the solution soon became pink, gradually darkening to purple and finally becoming almost black.

After the time stated 18 gms. Na_2CO_3 were added to neutralise the sulphuric acid, and the bulk of the acetic acid distilled off at 20° under reduced pressure. The residue was neutralised with Na_2CO_3 and distilled in steam. On redistilling the oily product, it was found to distil entirely below 120° / 10mm. A black resinous residue was left in the flask. No hydration had taken place.

Following the method of hydration described by Asahina and Tsukamoto [J. Pharm. Soc. Japan 1922, 463] 20 cc. Cedrene b.p. 120°/ 10mm. were dissolved in 16 cc. ether, cooled in a freezing mixture and 6 cc. $H_2SO_4.H_2O$ added slowly. The mixture was left for 3 days at room temperature, and treated as before. About 50 % yield of an oil was obtained b.p. 110°-120° / 10 mm. More distilled between 110°-115° than in the previous experiment.

The possibility of a product being volatile in acetic acid was realised, but on neutralising the acetic acid distillate and extracting with ether only the merest trace of oil was obtained.

A fresh sample of Cedrene was prepared b.p. 122°-123° / 10mm. The mixture of glacial acetic acid and sulphuric acid was made up as described in the first experiment, but as much Cedrene was added as the mixture would dissolve (40 cc.). This was kept at 50°-60° for 3 weeks, after which the oil was watered out. On distillation this oil gave about 30 cc. of an almost colourless oil b,p, 120°-125°/ 10 mm. The acetic acid layer was neutralised and steam distilled but yielded only about 1/2 cc. of an oil b.p. about 122°/10mm. The remainder decomposed above 160°.

On treating the product with a further quantity of sulphuric acid, the same changes of colour etc. were observed as before.

Another experiment was carried with a much stronger solution of sulphuric acid. 50 cc. Cedrene , b.p. 129°-131°/ 10mm. ; $d_{15}^{23.6}$ 0.9322 ; d_{15}^{15} 0.9391 ; $n_D^{25.8}$ 1.4995 ; n_D^{15} 1.5042 $[\alpha]_{Hg}^{19.5}$ -60.34° , were dissolved in 250 cc. glacial acetic acid and to this added 50 cc. $H_2SO_4.H_2O$. The addition of the sulphuric acid raised the temperature considerably, but no further heating was employed. The mixture turned a dark purple almost at once, and a quantity of Cedrene was thrown out of solution. The mixture was shaken mechanically for

6 hours, the oily layer separated (20cc.) and distilled. It had no smell of Cedrene b.p. 130° / 17 mm. d_{15}^{18} 0.9543 n_D^{21} 1.5000 ; n_D^{15} 1.5926 ; $[\alpha]_{Hg}^{195}$ -68.8°

The significance of these results has been dealt with in an earlier section of the thesis.

The purple colour of the acetic acid solution is immediately destroyed by water, but not by ether, in which the compound is insoluble. Incidentally it may be noted that there is practically no reaction between anhydrous acetic acid and caustic alkali, for having neutralised the sulphuric acid, the caustic alkali remains at the bottom of the flask unattacked, except as the solution absorbs moisture from the air.

Part II

The Action of Hydrogen Peroxide on Limonene.

The Action of Hydrogen Peroxide on Limonene.

The Hydrocarbon. d-Limonene is one of the most widely distributed hydrocarbons of the Terpene group, and was early recognised as a type of that large and varied class of substances known as the essential oils. As early as 1891, Wallach reported its presence in the oils obtained from certain members of the *Aurentaciæ*, in the oils of orange peel, lemon, bergamot, cummin, dill, fir needles and *Erigeron canadense*. Since then it has also been found in the oils of mandarin, neroli, petitgrain, ginger-grass, buchu leaves, caraway, celery, and from the oils from *Manila elemi, Macedonian fennel, Callitris glauca, Mondara punctata*, and in the fruits of *Pittosporum undulatum*.

Like many of its associates, it was re-named on several occasions, as the necessity of differentiating new substances demanded. So it happens that information on the chemistry of Limonene has first to be sought as a member of the Citrene group, the earliest reference being made by Gay Lussac and Larivière, Comp. Rend. 1841, *12*, 125) and by Hlaseweitz (Zeit. f. Chem [2], *4*, 380). By others the name Carvene was used, showing its connection with *Oleum Carvi*, and the name still persists for certain impure varieties, (Schweizer, Jour. f. prakt. Chem. 1841, *24*, 257). As the felationship of limonene to terpineol and dipentene came to be understood it received such names as Terpilene and Terpenylene but these very soon gave place to the names which the elucidation of these relationships have now permanently fixed.

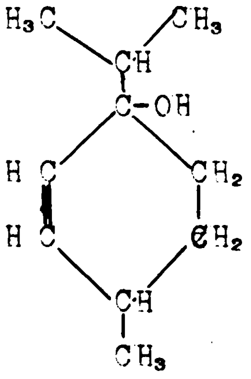
Always closely associated with the limonenes was the hydrocarbon which Boucharat called Dipentine (Comp. Rend., 1878, *87*,654 : 1880 , *89,* 361) from the fact that, on heating various essential oils, he obtained a pentane identical with isoprene. He further found that the change could be reversed, and that, by the application of heat, two molecules of isoprene united to give a hydrocarbon $C_{10}H_{16}$ which he therefore called Di-pentine. Following up this work, Tilden showed (Chem. News, 1882, *46,* 121 : J.C.S.,1884, *45,* 417) that this dipentine was identical with the optically inactive terpilene into which several of the terpenes and citrenes were convertible.

During the next decade progress was amazingly rapid. In 1886 Wallach published his third paper "*Zur Kenntniss der Terpene und der ätherschen Oele*"(Ann., 1885, *230,* 225), which defined the Terpenes as a group whose individual members were already partly recognised, and thereafter every year added new light on the relationships between the different hydrocarbons and their derivatives. From the point of view of the present work the above paper is interesting for its explanation of the relationship between the inactive dipentene and the already well known terpineol, and for the characterisation of terpin hydrate and its relationship to these two substances -- the three substances being interconvertible by the use of suitable hydrating and dehydrating agents. In the same paper the preparation of dipentene tetrabromide is also detailed. Since that time dipentene has been synthesised in several ways, and the relationship between it and numerous terpenes explained, yet the relationship between the optically active limonenes and the inactive dipentene remains in much the same position as Wallach left it after the publication of his two monumental papers " *Über Terpene und Campher,*" (Ber., 1891, *24*, 1525) , and"" *Zur der Terpene und der ätherischen Oele. I. Isomerieverhältnoise innerhalb der Limonene Reihe*" (Ann., 1892, *270*, 171) Chemically the d- and l- forms of limonene are identical, yielding the same derivatives which differ only in the direction in which they deflect a beam of polarised light. When mixed in equivalent proportions they give dipentene accompanied by the evolution of heat. The same result can be produced by the action of heat or by acids on either form of limonene. It must be observed, however, that while dipentene gives derivatives which correspond with those of the limonenes, these as a rule differ in melting point. Wallach found that even the boiling point of dipentene was higher than that of limonene by 3°, but it was shown (Tilden, J.C.S.,1893, *63*, T 292) that the preparation of dipentene from its dihydrochloride did not yield a pure product, but contained terpinene and terpinolene,and this was verified later by Wallach himself (Ber., 1907, *40*, 600) from a consideration of the yields of tetrabromide from dipentene prepared from the hydrochloride and from an equal amount of limonene. It would appear that the pure dipentene boils at the same temperature as limonene 175-176°. In almost every case the dipentene derivative can be obtained by mixing equivalent quantities of the d- and l-limonenes. The following table shows the differences in melting points recorded by Wallach in the papers cited above.

	Limonene Derivative M.P.	Dipentene Derivative M.P.
Tetrabromide	104-105°	124-125°
α.Benzoyl-limonene-nitroso-chloride	109-110°	90°
α.nitroso-limonene-nitrolanilide	112-113°	147°
β.nitroso-limonene-nitrolanilide	136°	129°
limonene-nitrolbenzylamine hydrochloride	103-104°	150°
limonene-nitrolanilide hydrochloride	117-118°	139-140°

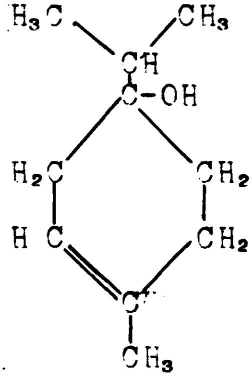
In view of these facts, which later work has only confirmed by adding others of a similar nature, It would appear impossible to regard dipentene as merely a physical mixture of the two isomers. Wallach suggested that the anomaly might be explained by assuming that dipentene was mainly composed of a third hydrocarbon ψ-limonene. It appears to the writer that a simpler explanation is to be found by assuming a loose double molecule to be formed when the two limonenes are mixed. The evolution of heat in this process demands such a reaction, but while it explains the difference in melting points, it must be admitted that it raises a difficulty regarding the molecular weight.

<u>The Constitution of Limonene</u>. The results which led to the elucidation of the constitution of dipentene, and hence of limonene, may be summarised briefly as follows. From physical considerations, Kannonikoff (J.Russ. Phys. Chem. Soc., 1883, *15*, 472) suggested that terpineol was a derivative of cymene, and assigned to it a formula, [I] remarkably near the truth when it is remembered that the chemistry of such compounds — partially unsaturated closed chains — was not at all understood ; cf. Reychler's highly theoretical discussion on the constitution of carvene (limonene), (Bull. Soc. Chim., [3] 7, 36) in which all the numerous formulæ suggested fall wide of the mark. Wallach (Ann., 1893, *277*, 105) suggested a slightly modified formula [II], while in the same year Baeyer (Ber., 1893, *26*, 2558) suggested a formula for terpin hydrate [III].



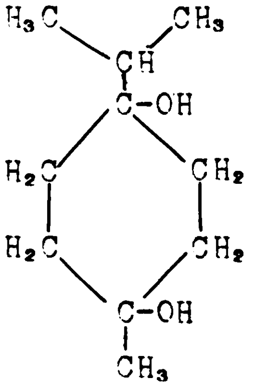
[I]

Terpineol
(Kanonnikoff)



[II]

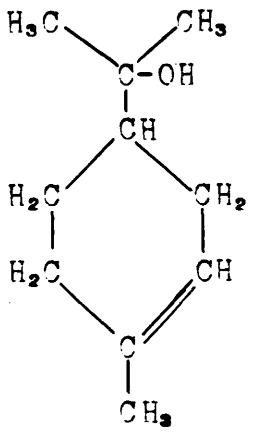
Terpineol
(Wallach)



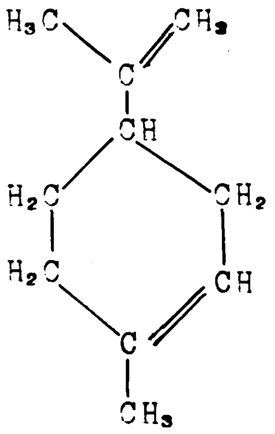
[III]

Terpin Hydrate
(Baeyer)

None of these formulae, however, explained the optical activity of the limonenes which were rightly believed to be identical in structure with dipentene. Baeyer's suggestion that the asymmetry was due to the molecule as a whole and not to an asymmetric carbon atom was not accepted (Ber., 1894, *27*, 454), and it fell to Wagner to solve the problem. In his historic paper " *Zur Oxidation cyclischer Verbindungen* " (Ber., 1894, *27*, 1636) he suggested formulæ for Terpenylic Acid, Pinol, Pinol Hydrate, Pinene, Terpineol, and Limonene, which have stood the test of subsequent research. His formulae for the last two are the now familiar



Terpineol
(Wagner)



Limonene
(Wagner)

In the following year Wallach confirmed the formula for terpineol, (Ber., 1895, *28*, 1776) by showing that when terpineol was oxidised it gave firstly Trihydroxy-hexahydro-cymene, then a keto-lactone, and finally Terpenylic Acid.[*] Absolute proof was lacking, however, until at least one of this closely related class of substances was synthesised. Bertram and Guildemeister had prepared terpineol and dipentene from geraniol as early as 1894(Jour. f. prakt. Chem. 1894, II, *49*, 195) by the action of formic acid, but a truly fundamental synthesis was not accomplished until 1904, when Perkin succeeded in preparing terpineol in the following brilliant way. [J.C.S., 1904, *85*, T. 654]

---

[*] Also Tiemann and Semmler (Ber., 1895, 28, 2141)

Ethyl.β.iodopropionate and Ethyl.disodio.cyano.acetate

$2(CH_2.I.CH_2.COOC_2H_5)$ + $C(CN.Na_2).COOC_2H_5$

gave

Ethyl.γ.cyano,pentane.α.γ.ε.tricarboxylic Acid

$(CH_2.CH_2.COOC_2H_5)_2.C.CN.COOC_2H_5$

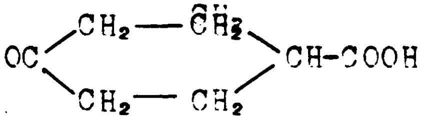
which, on hydrolysis with hydrochloric acid gave

Pentane.α.γ.ε.tricarboxylic Acid

$HOOC.CH_2.CH_2.CH(COOH).CH_2CH_2.COOH$

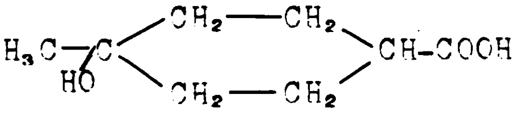
On digesting this with acetic anhydride and distilling, the ring was closed by removal of H_2O and CO_2 giving

δ.Keto.hexahydro.benzoic Acid



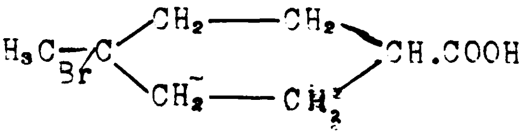
The ester of this acid was found to react readily with magnesium methyl iodide, giving on hydrolysis

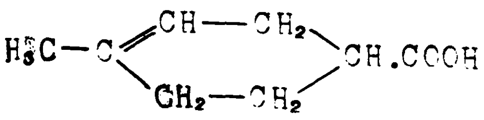
δ.Hydroxy.hexahydro.p.toluic Acid



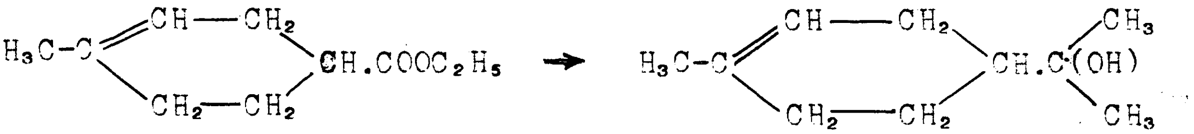
On treatment with fuming HBr followed by weak alkali there were formed

δ.Bromo.hexahydro.p,toluic Acid and Δ_3-Tetrahydro.p.toluic Acid



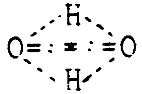


The last step in the synthesis was to convert the ester of this acid into terpineol by means of magnesium methyl iodide thus

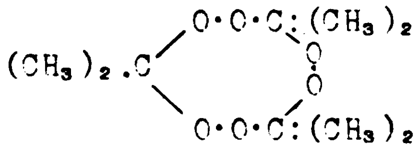


This agreed in every test with pure terpineol, and on heating this synthetic product with potassium bisulphate, dipentene was obtained by the elimination of water, and Wagner's formula for limonene finally proved correct.

The Oxidising Reagent. It was hoped that the comparatively mild action of Hydrogen Peroxide would avoid the perplexing intra-molecular changes to which terpenes are peculiarly liable on account of the very large number of closely related isomers which occur in this class of compounds. If this hope materialised, the knowledge of the action of this reagent on limonene, a substance whose constitution was definitely established, might prove of value in the elucidation of the much more problematical sesquiterpenes.

As an oxidising reagent Hydrogen Peroxide would appear to be almost ideal, being of the simplest composition, easily controlled and in no case recorded to be violent, and withal extremely convenient to handle. It is true that its constitution has not yet been definitely established, arguments having been advanced for at least three distinct formulæ (1) $H-O-O-H$, 12) $H-\underset{O}{O}-H$ and (3)  , [Willstater and Hauenstein, Ber.,1909, *42*,1839: A.Ruis y Miró, Hel. Chem. Act., 1920, *3*, 347, etc.]. Yet, however the affinities are arranged, and however the particular arrangement might affect the reaction, that reaction would be expected to be constant. Unfortunately it has been found, in most cases, that the conditions of the experiment played such an important part in the reaction that a wide variety of products were possible, and the reaction seldom proceeded in any one specific direction. Certainly such a fault might prove an advantage, as it indicated that a large range of products could be obtained if only the conditions could be regulated within sufficiently precise limits; but it is not surprising that a survey of the literature dealing with such a reagent fails to reveal any rule which would enable one to predict the course of the reaction in any particular case.

Wolffenstein was one of the first to be attracted by the reagent. Using acetone as a solvent he found that an acetone peroxide was formed to which he ascribed the formula



He investigated the action of Hydrogen peroxide through the medium of this acetone peroxide, on ring structures which contained a nitrogen atom, and found that the ring broke at the nitrogen and gave amido aldehydes (Ber., 1893, *26*, 2991 : 1895, *28*, 1459); and in some cases acids. Thus

Piperidine gave a mixture of formic, butyric and glutaric acids,

Copellidine yielded δ.amido.δ.methyl α.ethyl.valeraldehyde
$NH_2(CH_3).CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH(C_2H_5){\cdot}CHO.$

Coniine " δ.amido.δ.propyl.valeraldehyde.
$NH_2(C_3H_7).CH{\cdot}CH_2CH_2CH_2{\cdot}CHO.$

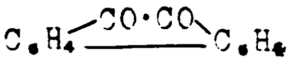
α.Pipeccline " amido caproaldehyde.
$NH_2(CH_3).CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CHO$

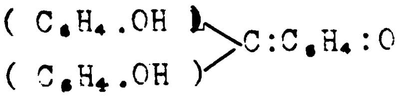
β.Pipecoline " δ.amido.β.methyl.valeraldehyde.
$NH_2.CH_2{\cdot}CH_2{\cdot}CH(CH_3){\cdot}CH_2CHO$

On the other hand with mesityl oxide a condensation took place. and after a considerable time he obtained a compound to which he gave the formula $HO{\cdot}C(CH_3)_2{\cdot}C(CO.CH_3).OH.\ C(CO.CH_3).OH.C(CH_3)_2OH$

Perkin also found this tendency to rupture the molecule in applying the reagent to the oxidation of α.α.ketones (J.C.S., 1907, P. 23, 166). Thus

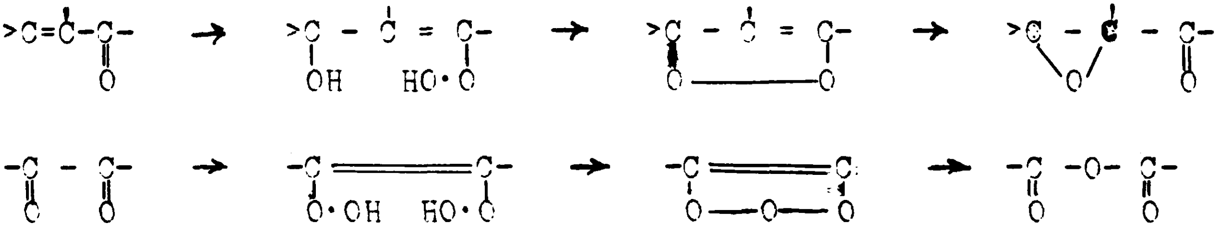
Benzil $C_6H_5.CO{\cdot}CO.C_6H_5$ yielded benzoic acid

Phenanthraquinone 
$C_6H_4 \overset{CO\cdot CO}{\longrightarrow} C_6H_4$ gave diphenic acid and an unidentified liquid

Aurin 
$\begin{matrix}(C_6H_4.OH)\\(C_6H_4.OH)\end{matrix}\!\!>C{:}C_6H_4{:}O$ gave p.hydroxy-benzoic acid and benzoquinone (through quinol)

In applying the reagent to the oxidation of substances with phenolic groupings the author found that the oxidation could be carried out without the necessity of protecting the hydroxyl radicle by methylation. He employed acetic acid as solvent, but while beneficial, did not consider it essential to the reaction.

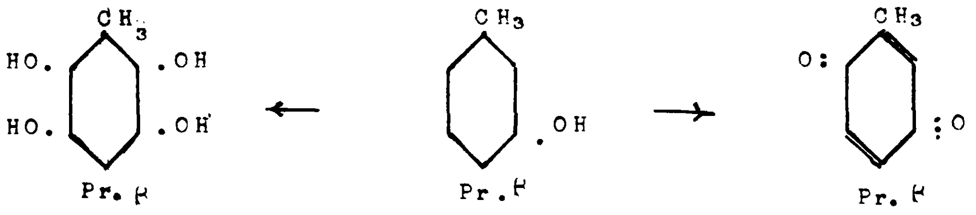
As the result of their work on α.β.ketones Weitz and Scheffer [Ber., 1921, *54*,*B*, 2337], suggest the mechanism



Thus in Wolffenstein's work the reagent reacted simply as an oxidiser, breaking the ring formation and giving an aldehyde. In the case of mesityl oxide two hydroxyls were added at the double bond, while two hydrogens were removed or oxidised away causing the condensation of two molecules. In Perkin's work the action was also one of normal oxidation, diketones being converted into ~~converted into~~ dicarboxylic acids with a rupture of the bonds joining the two ketone radicles. Another type of oxidation was shown to take place by Wieland,* who converted acetic acid into glycollic acid and the carbonic acid of bicarbonates into formic acid.

In the course of a very extensive investigation of the behaviour of this reagent (J.C.S., 1910, *97*, T.1659) Henderson and Boyd have recorded the products of a large number of phenols as follows

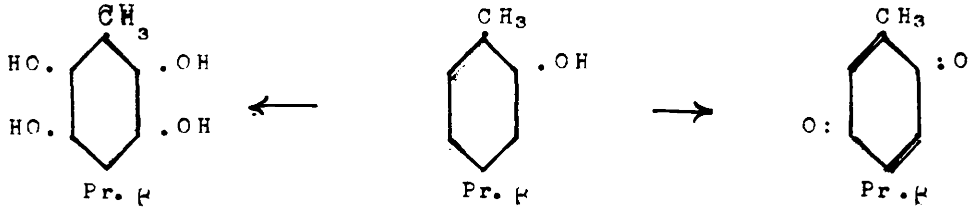
[*Wieland, Ann.,1924, 436,229.]



Tetrahydroxy-cymene.

Thymol.

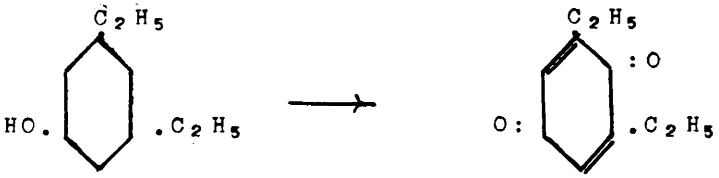
Thymo-quinone.



Tetrahydroxy-cymene

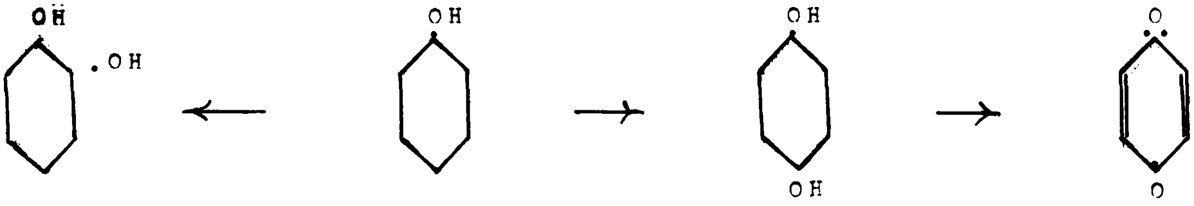
Carvacrol

Thymo-quinone



Diethyl-phenol

Diethyl.p.benzoquinone

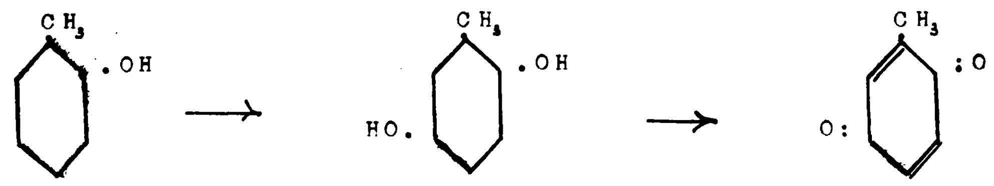


Catechol.

Phenol

Quinol

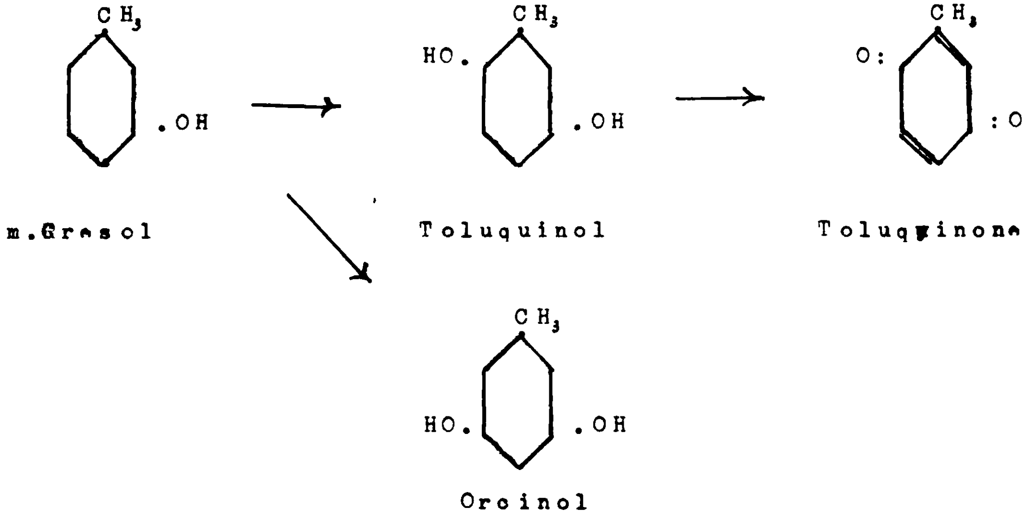
p. Benzoquinone.

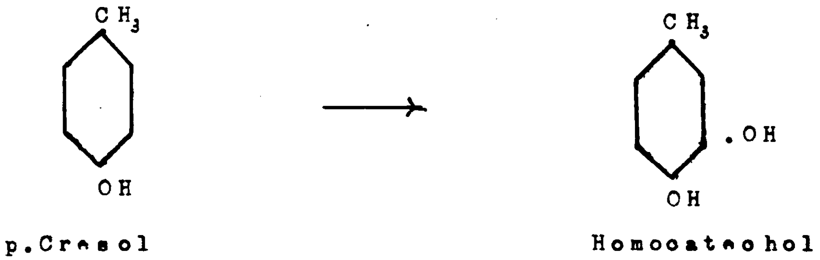


o.Cresol

Toluquinol

Toluquinone





Benzene, Toluene, 1:3.diethylbenzene, and cymene did not react, but Naphthalene gave Phthalic Acid, Anthracene gave Anthraquinone, and Phenanthrene gave Phenanthraquinone.

As a result of these experiments the authors concluded that the character of the oxidation products depended in the first place on the constitution of the phenol to be oxidised and in the second place on the conditions of the experiment viz:- the proportions of H_2O_2 used, the concentration of the acetic acid solution, on the temperature and on the time allowed.

The position of the side chains with reference to the hydroxyl affected both the vigour of the reaction and the products. Thus a radicle or side chain in the para position to the hydroxyl caused the reaction to proceed with greater difficulty, and gave as a rule a dihydric phenol, the second hydroxyl being in the ortho position to the first. If the side chain occupied a position other than the para, the reaction went more easily and the products were mainly a quinone and a p.dihydric phenol.

Applied to the terpenes, the action of hydrogen peroxide has been found to be so much regulated by the structure of the substance undergoing oxidation, and by the conditions of the experiment that the products are of an extremely complex nature, often difficult to isolate, and often showing that intermolecular changes have taken place much more extensively than the mild nature of the reaction would lead one to expect.

Thus, among the numerous products from Camphene there were found in addition to the main products $C_9H_{15}.COOH$ (Camphylic acid) and $C_9H_{14}O$ (Camphenilone), $C_9H_{15}.CHO$ (Isocamphenilaldehyde), a substance $C_9H_{16}O_2$, and $C_{10}H_{16}(OH)_2$ (Camphene glycol) and other substances which were not identified (Henderson and Sutherland, J.C.S., 1911, *99*, T.1539).

α.Pinene gave α.Terpineol, Borneol, Dipentene, Menthene.1:4:8.triol, and a trace of an aldehyde (Henderson and Sutherland, J.C.S., 1912, *101*, T.2288)

β.Pinene, on the other hand, gave only Borneol and Fenchyl alcohol, and other substances not identified.

It would be expected that if hydrogen peroxide were correctly represented by the formula H·O·O·H , that it ought to have proved a valuable reagent for the location of double bonds, since it would be expected under normal conditions to yield a glycol. In the numerous examples cited , however, this is not supported. Moreover, only one molecule of the reagent would be required for every atom of oxygen introduced; whereas in every case at least two molecules were required. That the addition of a second molecule did not simply continue the oxidation another stage was shown by the fact that the use of less than two molecules left some of the original substance unattacked, and the products were of the same nature,

In this connection the work of Prileschaäeff (Ber.,1909, *42*, 4811) is of great interest. In place of hydrogen peroxide he used benzoyl-hydroperoxide $C_6H_5.CO\cdot O\cdot OH$, to oxidise hydrocarbons etc., and obtained a series of oxides and dioxides, which, on hydration, yielded di-hydroxy and tetra-hydroxy derivatives as shown in the following table.

Terpene	Oxidation Product	Hydration Derivative.
Geraniol	Geraniol Oxide	
$C_{10}H_{18}O$	Geraniol Dioxide	Triol-oxide
Linalool	Linalool Oxide	Aldehyde
$C_{10}H_{18}O$	Linalool Dioxide	Triol-oxide
Limonene	Limonene Oxide	Glycol (m.p. 66-67°)
$C_{10}H_{16}$	Limonene Dioxide	Erythritol (b;p; cir.220°)
Pinene	Pinene Oxide	Sobrerol (m.p. 150°)
$C_{10}H_{16}$		

Although the reaction in the case of benzoyl hydroperoxide cannot be assumed to proceed in a manner exactly analogous to that of hydrogen peroxide - on account of the unsymmetrical constitution of the former compared with the latter- , the fact that the results quoted above indicate that the reaction is really one in which an oxy- and not a hydroxy- compound is the first product cannot be disregarded, and its bearing on the present work on Limonene will be discussed later (p. 95).

The action of certain other oxidising agents are also of interest and it will be convenient to mention these before proceeding to a detailed account of the action of Hydrogen Peroxide on Limonene.

Potassium permanganate has been extensively employed to give an oxidation series with very considerable success. Using a 1% alkaline solution, Wagner succeeded in preparing a tetrahydric alcohol, m.p. 191·5–192° (Ber., 1890, *23*, 2315). Later Ginzberg,(*) working on the oxidation of Sobrerol with this reagent, prepared a glycol from trihydroxy-menthene which he found to be $\Delta^{8(9)}$ menthene.1:2 diol m.p. 63–64° ; on oxidising this substance with $KMnO_4$ he obtained a tetrahydric alcohol which melted at 169°. One would have expected this to have been identical with that obtained by Wagner, while the glycol is undoubtedly that described in the present research m.p. 67·5°. Stronger solutions of the reagent were found to break the ring giving acids etc.

The action of chromyl chloride is dealt with elsewhere in this thesis and has no special bearing on the present work.

(*) Ginzberg, Ber., 1896, 29, 1200.

On exposure to light and moist air for a prolonged period (a process described in the literature as auto-oxidation) Blumann and Zeitschel (Ber., 1914, 47, 2623) obtained carvone, carveol, and a white solid which melted about 60°. There is little doubt that this last was an impure specimen of the glycol obtained in the present research.

Very recently a substance was isolated from the oil of lemon by Romeo (Annali Chim.,Appl., 1925, **15**, 305) which would appear to be the optically active isomer of this glycol.

The Action of Hydrogen Peroxide on Limonene.

The d-limonene used in this investigation was obtained by the fractional distillation of *Oil of Bitter Orange* which had been purified by washing with alkali and subsequent distillation in steam. In the selection of the particular fraction, use was made of a graph (p116) in which the optical rotation of fractions were plotted against their boiling points. The almost perpendicular nature of this graph between the temperatures 176·5° and 177·5° shows that at this point a definite constituent is to be found (cf. A similar graph for *Cedrene* p. 6) The physical constants of the purifed hydrocarbon were B.P. 175·5–176·5°C (corrected) / 759mm. $[\alpha]_D^{18^\circ}$ +96·89° ; $d_{15^\circ}^{15^\circ}$ 0·8458 ; $n_D^{15^\circ}$ 1·4759.

The hydrogen peroxide used was Merck's *30% Perhydrol*. Previous work showed that the reaction between this reagent and the terpenes in acetic acid solution proceeds smoothly and without vigour, and in consequence of this it has been customary to carry it out at a slightly elevated temperature (about 60°), using an excess of reagents. This procedure was repeated as described on p.*103*, two molecular proportions of perhydrol being used in an excess of glacial acetic acid in the hope that each molecule of peroxide would attach itself to a double bond and give a tetrahydric alcohol. The reaction, however, followed an entirely different course. The main product consisted of a variety of substances, from which, after hydrolysis, a crystalline glycol was finally isolated. Only a small yield of this substance was obtained, but in an endeavour to obtain a more satisfactory yield, the conditions controlling the reaction were investigated, and an improved method evolved which yielded about 40% of the glycol. This method has been applied by other workers in this laboratory with much success.

Investigation of the Conditions governing the Reaction, and the Deductions from the Results.

While limonene is completely miscible with glacial acetic acid, its solubility decreases as the acid is diluted: the oxidation products, on the other hand, are soluble in the moderately dilute acid. These facts gave an obvious and convenient method of observing the progress of the oxidation.

Effect of the area of contact on the rate of the reaction.

That physical conditions exercise a marked effect on the reaction was shown while carrying out several trial experiments, e.g. an experiment using 10gms. of limonene was complete in about 40 hours while a repeat using 50gms. was not complete in 3 weeks. As the addition of perhydrol caused the hydrocarbon to separate completely, it was concluded that the difference in the rate of reaction had been largely due to the difference in surface contact. This was confirmed in two controls (p.104) in which the rate of reaction in that with a contact surface about double the other was almost twice that of the latter. The increase in the rate of the reaction caused by raising the temperature was due not only to the resulting increase in vigour, but also to the increase in the solubility of the hydrocarbon in the acetic acid-perhydrol layer.

Effect of a gradual addition of Perhydrol

It was observed that the solubility of limonene in acetic acid diluted with perhydrol was not a linear function of the dilution, but decreased very rapidly when perhydrol equal to about one third of the volume of acetic acid had been added. It was therefore thought advisable to add the perhydrol gradually in order that as much of the hydrocarbon might be kept in solution as possible. This was found to be highly satisfactory, as the hydrocarbon was presented to the oxidising agent in solution, and in consequence the reaction only became sluggish after about one molecular proportion of perhydrol had been added. The gain in time was considerable and the solution did not darken in colour on heating, even to 80%C, as it did when all the perhydrol had been added all at once.

The rôle of acetic acid in the reaction.

In the traditional method it was assumed that the acetic acid acted as a solvent only, excess being used to keep the hydrocarbon in solution (Henderson and Boyd, J.C.S., 1910, *97*, T.1659), and while beneficial was not essential to the reaction (Perkin, J.C.S, 1907, *23*, P.166). While acetic acid, as such, is probably not essential, the results of the following investigation would appear to prove that it does play a more essential *rôle* than that of solvent.

If the acetic acid were merely a solvent, the first part of the reaction should proceed with a small quantity of solvent provided the perhydrol were added in very small quantities, for the bulk of the hydrocarbon is then still in solution. It was found, however, that using 30cc. of acetic acid for 100gms. of limonene no oxidation had taken place at the end of a fortnight, nor did the further addition of 40cc.acetic acid improve the reaction.

The controls used in the investigation of the effect of surface contact were again brought into requisition. The control with the smaller surface contact had lagged, but on the addition of acetic acid it not only made up what it had lost but gained on the control with the advantage of a larger contact surface. On uniting the two controls and adding sufficient acetic acid to keep the hydrocarbon in solution the reaction completed itself in 24 hours.

Using 100gms. of limonene and adding the acetic acid and the perhydrol gradually, the progress of the reaction was observed, when it was found that practically no oxidation took place until about 230cc. of acetic acid had been added. Details of this experiment will be found on p.106.

If the acetic acid were indeed a catalyst, the addition of more acetic acid should accelerate the reaction still further. This was actually found to be the case, and the reaction to be more than half-completed in 18 hours. (see p.106). A still greater excess allowed the reaction to be almost completed in 19 hours (see p.107). These experiments were all carried out between 60° and 70°.

From these results the conclusion would appear inevitable that hydrogen peroxide has itself little or no action on the hydrocarbon, but reacts through the medium of a compound which is decomposed by water but more stable in an excess of acetic acid. The compound is most probably aceto-hydro-peroxide. Hence, when solvents such as ether or dilute acetic acid are employed there is no reaction. Other substances could be substituted provided they could play the part of catalyst. This would explain why Wolffenstein (supra) found acetone satisfactory, since it gave acetone peroxide. Iron salts were used successfully as catalysts[Hopkins and Cole, Proc. Roy. Soc., 1901, 68, 21 ; Neuberg, Biochem. Zeitsch. 1914, 67, 71 and 127 : Mummery, J.S.C.I., 1913, 32, 889], although the reaction was found to proceed in acetic acid solution even in the absence of iron salts. Again Prileschäaeff conducted his investigations in ethereal solution with complete success, but he employed, not hydrogen peroxide, but its derivative benzoyl-hydroperoxide, which, having itself the characteristics of the previous intermediary compounds, required no activating solution.

The fact that two molecular proportions of perhydrol were required, and that no evidence of a tetrahydric alcohol was obtained, showed that the reaction was not one of simple addition of the ruptured molecule of hydrogen peroxide. It might be suggested that the excess molecule of peroxide is required to establish the equilibrium necessary for the reaction, for there is no indication of free oxygen being liberated until more than one molecule of perhydrol has been added, but neither of the arguments are specific.

As the result of these investigations it was decided to conduct an oxidation at room temperature using a quantity of glacial acetic acid somewhat in excess of that required to ensure the completion of the reaction in a reasonable time. To do this efficient mechanical agitation was necessary. This proved very satisfactory. As the yield of glycol was much improved by this method, it was thought that a further addition of perhydrol would ~~would~~ give the tetrahydroxy derivative. No agitation was required as the addition of two molecules of perhydrol results in products which are completely soluble in the acetic acid present. The experiment, however, was quite unsuccessful, resulting in a product, which although clear and colourless, was entirely resinous.

Products of the Reaction.

On occasion a small quantity of terpin hydrate was obtained in the course of oxidation. This could be crystallised from the ethereal solution of the oxidation products. The main product consisted of an oil which contained a number of derivatives. Part appeared to be soluble in water, but on attempting to separate the soluble from the insoluble portion, the oil emulsified and rendered this method of separation useless. Exhaustive treatments with sodium bisulphite and with semicarbazide hydrochloride gave only a trace of ketone (or aldehyde) ,too small to be identified With the latter reagent a yellow amorphous substance separated. This crystallised from water in well defined yellow cubes and in irregular flakes according to conditions. It was found to be insoluble in alcohol, and was a product of the polymerisation of semicarbazide. Distillation in steam, before and after hydrolysis with alcoholic potash, gave no satisfactory result, as the oils obtained were as complex as the original product, the process of distillation causing partial decomposition. The larger portion was distillable in steam. It was unsaturated and gave on analysis

C = 71.99 ; H = 9.86 % .

When the products, after hydrolysis, were distilled at reduced pressure more definite results were obtained (details on p.111-112). In addition to very small quantities of low boiling oils, smelling of eucalyptus and peppermint etc., three fractions, differing widely in viscosity, were separated, but repeated fractionation failed to give any well defined fraction and caused considerable resinification. The three fractions were roughly as follows:-

(1) A clear, pale yellow, mobile liquid B.P. 110-112° C/ 10mm.

(2) A clear viscous liquid B.P. 140-143°C /10mm.

(3) A vitreous semi solid, B.P. 150-153°C/10mm.

In addition to these, a small quantity of a solid condensed on the end of the condenser in the form of a white snow. It distilled over about 180°/ 10mm. just before decomposition began and liquified immediately the vacuum was broken.

All three fractions gave sodium derivatives, which on analysis gave results which corresponded to one and two hydroxyl groups in the molecule. They were all unsaturated, the unsaturation decreasing as the boiling point of the fraction increased.

Fraction	% Na in Sodium Derivative	% Na required for
110-112°C/ 10mm.	9.5	$C_{10}H_{16}(ONa)_2$ = 21.3% $C_{10}H_{17}.ONa$ = 13.0%
140-143°C/ 10mm.	22.7	
150-153°C/ 10mm.	16.1	

From these results it would appear that the middle fraction is almost entirely composed of a dihydroxy derivative. That the result is high is not surprising, for it is impossible to exclude water completely in the preparation of these highly hygroscopic substances: this produces caustic soda and a correspondingly high result for Na in the sodium derivative. It would further appear that the lowest fraction contains secondary products, or at least products without a hydroxyl group, and that the highest fraction is mainly a hydrated compound, i.e. it has been formed by the addition of H_2O and has the formula $C_{10}H_{17}.OH.$, but contains a certain quantity of the dihydroxy compound of the middle fraction.

From the middle fraction $\Delta^{8(10)}$p.menthen.1:2 diol was finally obtained in rather a novel way. In order to induce crystallisation, all conceivable solvents had been used, both in the anhydrous condition and when suitably diluted with water; even liquid air had been used without result. On treatment of the oil recovered from the preparation of the sodium compounds with acetic acid, small crystals were obtained, which again liquified on drying in a vacuum desiccator. This was thought to be due to the loss of water of crystallisation, and so it proved to be, for on rubbing the viscous liquid with a rod moistened with water crystals were again formed. Thereafter they were readily obtained from aqeous solution, especially if a little benzene were added to float off adhering oily products.

An attempt to isolate the product of hydration, indicated in the highest fraction, was only partly successful. HBr was passed into an ethereal solution of the oil which remained after the glycol had been removed. A crystalline derivative was obtained and purified from ethyl alcohol (methyl alcohol hydrolyses it). It was somewhat unstable and only two recrystallisations were possible. It melted at 44-45°C. and contained 53·5% Br. ($C_{10}H_{18}Br_2$ requires 53·64% Br.)It was expected that dipentene dihydrobromide would be formed, but the compound could not be found in the literature.

As the substance from which this compound was prepared was unsaturated, and presumably not a hydrocarbon, it must be concluded that the original substance had the formula $C_{10}H_{17}.OH$, $C_{10}H_{16}$ and $C_{10}H_{18}(OH)_2$ being ruled out for the two reasons given).

Repeated attempts to prepare a phenylurethane only gave diphenyl-urea m.p.238.5° . N = 13.40% ,;$(C_6H_5.NH)_2.C{:}O$ requires N = 13.21% .

Attempts to prepare a nitrobenzoate were almost as unsuccessful. Only on one occasion was a small yield obtained. After purification, it crystallised in light flakes with a strong silvery lustre. It melted at 79°.

Terpin Hydrate. This substance is well known, but the following properties do not appear to have been previously mentioned. The substance is readily volatile in alcohol. If a solution in alcohol be allowed to evaporate rapidly in a flask stoppered with cotton wool, long needles of terpin hydrate suspend themselves from the cotton wool. Distillation of an alcoholic solution is thus an obvious andconvenient way of purifying the substance. Owing to its tendency to sublime, the melting point is not easily observed and must be done in a sealed tube.

The Glycol. Analysis of this substance gave C = 70.62 ; H = 10.51% , $C_{10}H_{18}O_2$ requires C = 70.57, H = 10.68% . It is unsaturated and when thoroughly dehydrated melts at 67·5°C. It is clearly the product of Prileschäaeff (p.88) . It is almost certainly the "solid" obtained by Blumann and Zeitschel (Ber., 1914, 47, 2623), and likewise the glycol described by Ginzberg, (Ber., 1896, 29, 1200). It is therefore $\Delta^{9(10)}$ p.Menthen.1:2 diol. It crystallises from water, in which it is soluble to about 10% , in pearly flakes, which effloresce in air and contains 3 H_2O in the crystalline form; these can be completely removed in the course of several days in a vacuum desiccator over sulphuric acid. The substance melts to a clear liquid which is appreciably volatile at 100°, at which temperature it is slightly volatile and soon becomes discoloured. It is even slightly volatile in a vacuum desiccator, as shown by the continued discolouration of the sulphuric acid in the desiccator and the steady loss in weight which accompanies continued desiccation.(see p.114). Its solution in alcohol is optically inactive, and in this respect differs from what is almost certainly the optically active form of the glycol described by Romeo (p.90).

Part II.

Experimental.

EXPERIMENTAL.

Preparation of the Hydrocarbon.

Oil of Bitter Orange was washed four times with a dilute solution of NaOH to remove acids, and then with water - a large excess prevented emulsification - until all trace of alkali was removed. The resulting oil was freed from resinous material by distillation in steam. This gave a clear colourless oil, which was dried over $CaCl_2$ and distilled with fractionating column. The first distillation was collected in two fractions, " below 170° " and"170°-185° " . These were redistilled in fractions, 170°-175°, 175°-178°, 178°-180° . On redistillation, fractions were taken at each ½°, starting at 175° / 759 mm. The Optical Rotations of the fractions were as follows.

Fractions	Mean Values $[\alpha]^{18}_{D}$
176°	+ 94.83°
176.5°	+ 94.69°
177°	+ 96.60°
177.5°	+ 97.57°
178°	+ 98.34°

The graph of these results (p116) shows that the Limonene is to be found in the fractions between 176·5° and 177·5°. In the final distillation, these fractions only were retained

The thermometer was not totally immersed. The corrected reading would be 175·5°–176·5°. The rotation of the redistilled sample was + 96·89° (mean of six readings) The other constants were $d_{15}^{15^\circ}$ 0·8453, $n_D^{15^\circ}$ 1·4759.

Oxidation of Limonene.

In the oxidations glacial acetic acid was used as solvent and hydrogen peroxide was added in two molecular proportions, and the whole allowed to react at a temperature about 60°, until the layer of hydrocarbon had entirely disappeared. The time taken for this reaction varied within a wide range, and experiments were carried out to discover the cause.

A trial experiment with 10 gms. Limonene was complete in 4 40 hours. A repeat with 50 gms of the hydrocarbon had not completely reacted after 3 weeks. The addition of more perhydrol did not effect the oxidation desired. The only conclusion which could be drawn from these results was that the hydrocarbon was thrown out of solution by the addition of the perhydrol, and that the reaction thereafter was extremely slow, being dependent on surface contact. In the trial experiment this would be very much greater.

It was thought that the gradual addition of the perhydrol would overcome this difficulty, as the hydrocarbon would be retained in solution until the reaction was well advanced. Its application was entirely satisfactory, the reaction going rapidly at first, and only becoming sluggish after about one molecular proportion of perhydrol had been addedl The gain in time was considerable and the solution did not darken even on heating to 80° and over, as it did when the perhydrol was added all at once.

As the gradual addition of the perhydrol had been successful in reducing the time of the reaction it was thought that it might be used to reduce the excessive amount of acetic acid required for the reaction. The proportions used were $C_{10}H_{16}$, 100 gms., $CH_3.COOH$, 240 cc., H_2O_2, 160 cc. To test this 100 gms. of Limonene were dissolved in 30 cc. glacial acetic acid and 20 cc. perhydrol added gradually during the course of a fortnight. Practically no oxidation took place. The further addition of 40 cc. acetic acid and 60 cc. perhydrol did not produce any appreciable result.

The influence of the area of surface contact on the rate of reaction was now investigated. The above mixture was divided into two portions; one of which was placed in a 1 litre flask, and the other in a ½ litre, and kept under similar conditions. The volumes of the layers were measured at intervals. The results show that the reaction, although slow, is appreciably affected by the extent of the contact surface. The amount of solvent was now increased in the smaller flask with the result that it made up in a night what it had lost in a week and actually gained on the other. This shows conclusively that the rate of the reaction is dependent on the intimacy of contact.

Effect of Contact on the Rate of Reaction.

Time between Observations.	Temp.	In 1 Litre Flask		In ½ Litre Flask.	
		Volumes of Layers	Vol. of Limonene oxidised	Volumes of Layers	Vol. of Limonene oxidised
4 days	50° 20°	40cc. 78cc. 32cc. 85cc.	8cc.	40cc. 78cc. 34cc. 84cc.	6cc.
Added 40cc. H_2O_2 to each.					
3 days	50° 20°	33cc. 124cc. 24cc. 132cc.	9cc.	34cc. 122cc. 29cc. 126cc.	5cc.
Added 10cc. $CH_3.COOH$ to ½ Litre Flask.					
1 day	53° 20°	24cc 132cc. 23cc. 133cc.	1cc.	29cc. 136cc 21cc. 144cc.	8cc.

On experiment it was found that while the hydrocarbon can be dissolved in acetic acid and thrown out with water, the products of oxidation remain in solution, being soluble in acetic acid diluted to a considerable extent with water. The volume of the hydrocarbon layer is therefore an excellent measure of progress of oxidation.

The above experiments were again united and sufficient acetic acid added to keep the hydrocarbon in solution (a total of 270cc.) After 24 hours oxidation was found to be complete.

A confirmatory experiment was carried out, adding the two reagents gradually and observing the progress of the reaction

Time between Observations	Vol of $CH_3.COOH$	Total	Vol of H_2O_2	Total
	30cc.	30cc	20cc	20cc
1 day		30 "	5 "	25 "
2 days	10 "	40 "	10 "	35 "
5 days	10 "	50 "	10 "	45 "
6 days	30 "	80 "	20 "	65 "
8 days	50 "	130 "	-	65 "
3 days	50 "	180 "	-	65 "
2 days	50 "	280 "	30 "	95 " (*)
10 days	20 "	250 "	20 "	115 "

(*) The reaction, up to this point very slow, began to increase rapidly.

There was now no doubt that the acetic acid was more than a solvent, and if so, something more than that required to allow the reaction to proceed should increase the rate of the reaction still further. This was found to be the case as shown below

Time	Volume of Limonene Layer.
	60cc.
18 hours	35 "
3 days	18 "
1 day	18 " (added 10 cc H_2O_2)
1 day	5 cc.
1 day	5 cc.

Further evidence of the essential rôle which the acetic acid plays in the reaction was obtained in an attempt to use ether as solvent. 10cc of Limonene were treated with 5cc. $CH_3.COOH$ and 10cc. H_2O_2 in 30cc. ether (the $CH_3.COOH$ was added as a catalyst). It was hoped that as ether is appreciably soluble in water it would retain some of the hydrocarbon in the perhydrol layer, and thus remove the necessity of the excess of acetic acid. The experiment was entirely unsatisfactory, from that point of view.

On the other hand a still more liberal excess of acetic acid allowed the reaction to be completed in less than two days. 50gms. $C_{10}H_{16}$, 50cc. H_2O_2 (instead of 80cc.) and 160cc. $CH_3.COOH$ (instead of 125cc.) wre allowed to react at 60°

Time	Volume of Acetic Acid Layer	Volume of Limonene Layer
	195cc.	53cc.
6 hours	217 "	31 "
19 "	239 "	5 "
22 "	244 "	0 "
47 "		

In all these experiments the traditional temperature,,60°, was used. The yields, however, were poor, and it was found much more satisfactory to carry out the experiment at room temperature. For this to be successful mechanical agitation was essential and as the hydrocarbon is less soluble in the slightly diluted acetic acid at room temperature than at 60° more acetic acid was required. The following is an example of a "cold" oxidation. 100 cc. Limonene were dissolved in 375 cc. glacial acetic acid, and perhydrol added, in 20 cc lots at intervals, to a total of 180 cc. In 12 hours the reaction had just begun; at the end of a week about 65 % of the Limonene had been oxidized, in 10 days only about 5 to 10 cc remained unattacked, which required from 4 to 8 days to oxidise. The whole oxidation therefore occupied from 14 to 18 days, instead of 2 days in the oxidation at 60°; on the other hand the yield of definite product was increased from 4 to 40 %.

From half of the above the products of oxidation were extracted as will be described later. The other half was treated with more acetic acid and an excess of peroxide in the hope that a tetrahydrate or erythritol would be produced. As the addition of perhydrol no longer caused the formation of a double layer, no agitation was necessary. The solution was allowed to stand for a fortnight. There was still an excess of perhydrol present as shown by the pressure of escaping oxygen in the flask. As the result of about 40 extractions an oil was collected (about 80 % of the possible yield). Even cold aqeous $Ba(OH)_2$ resinified this oil completely.

Extraction of the Oxidation Products.

To the solution in acetic acid, contained in a flask of two litres capacity and fitted with a delivery tube passing into a wash bottle containing Na_2CO_3, there was added a strong solution of Na_2CO_3 until the acid was just neutralised. The solution was used instead of the crystals as the latter causes the formation of solid sodium acetate, and is also liable to cause violent frothing towards the end of the neutralisation. The solution could be controlled much more easily. When cold the neutral solution was thoroughly extracted with ether. As a rule from 8 to 10 extractions were necessary but sufficient; on one occasion as many as 40 extractions were required, but the products in this instance were resinous. The ethereal solution was dried over sodium sulphate.

On concentrating this solution, crystals of terpin hydrate separated on one occasion. The melting point of this substance is difficult to obtain owing to the fact that it sublimes. Using an ordinary melting point tube it was found that the melting point varied from 102° to 112°, and repeated crystallisations did not raise it. In a sealed tube it melted at 116-117°. On analysis it gave

C = 62.84% H = 11.53% : $C_{10}H_{18}(OH)_2$ requires C = 63.10% : H = 11.66%.

Complete removal of the solvent left a yellow, viscous oil having a sweet smell suggestive of an ester. It was treated exhaustively with $NaHSO_3$ (made by passing SO_2 into Na_2CO_3 solution until supersaturated, allowing to cool and using the supernatant). The mixture was allowed to stand for several weeks with occasional shaking. Crystals were deposited. These were washed, with alcohol and ether, decomposed with sodium carbonate and distilled in steam. The distillate, however, only yielded the merest trace of aldehyde.

Treatment with semicarbazide acetate (made by mixing a concentrated solution of semicarbazide hydrochloride with a solution of the equivalent amount of potassium acetate in alcohol and removing the precipitated KCl.) gave indications of a solid derivative, and a thorough trial was made. As the removal of the alcohol necessitates a distillation, it was thought advisable to test the value of distillation in steam as a method of separating the products. The neutral product was treated with an excess of semicarbazide acetate and allowed to stand for about three weeks, at about 60°. At the end of that time some sodium acetate and potassium chloride had separated out along with a quantity of a yellow solid. This was found to be insoluble in alcohol and ether but slightly soluble in water, from which it could be crystallised in regular cubes and fine flakes. It melted at 245-246°. Found N = 40·7%. a value which does not agree with the semicarbazone of a mono-ketone or with that of a di-ketone which require respectively N = 21·1, and N = 31·1% . It is clearly a product of polymerisation of semicarbazide itself. The residual alcoholic solution was distilled in steam to remove the solvent: a small quantity of oil was also carried over. The remaining oil had separated into two layers, a part being soluble and a part insoluble in water. These were distilled in steam, and the resulting oils hydrolysed. In every case, there was obtained a neutral product, a brown resinous viscous acid, and a thick resin. The yields were very poor and the products no more easily isolated than the original oils.

The amount of aldehyde or ketone being negligible, these treatments were not repeated.

The neutral product from the hydrolysis of the oil was distilled. A drop of clear oil distilled at 98°C/ 759 mm. and smelt of eucalyptus. The distillation was then conducted at reduced pressure giving at 18mm. the following fractions,

Boiling Point 18mm.	Description
60°	A very mobile oil (small quantity)
60-160°	" "
160-180°	A viscous, but clear and colourless oil
180- 200°	A clear but semi-solid product.
280°	A white snow which liquified on breaking the vacuum. (a drop)

There was no stationary boiling point during the distillation. That a rough separation had been achieved was shown by the difference in viscosity, and the method was applied to a fresh quantity of the oxidation product after hydrolysis with methyl alcoholic potash.

About 50% of the oxidation product resinified in the process of hydrolysis: of the remaining 50%, about ¼ distilled below 120/10mm.

another ¼ between 120-160° / 10mm., and ⅓ between 160-200° / 10mm. The last fraction showed a cleavage like a resin, which disappeared on standing. On distilling these fractions several times under reduced pressure, considerable resinification took place and the lower and higher fractions tended to disappear. The fractions finally became at 10mm.

Boiling Point	Description.
70-80°	A drop of a clear liquid
90-110°	A clear mobile liquid (small quantity)
110-135°	" "
135-145°(142°)	A clear viscous liquid.
145-170°) 152°)	A more viscous oil
170°-	A resin.

In the hope of obtaining a crystalline substance from at least one of these fractions all kinds of solvents were used including benzene, petroleum ether, acetone, carbon tetrachloride, water , alcohols, ethyl acetate, acetic acid. The solvents were allowed to evaporate slowly. They were diluted, left for periods in a freezing mixture, and in an ice chest. Even liquid air was tried as a means of inducing crystallisation, but without result.

As mentioned in a previous section the process of fractional distillation under reduced pressure failed to separate the constituents of the oil after hydrolysis, but it at least showed that there were three constituents present - a mobile oil B.P. about 110°/ 10mm. ; a viscous liquid B.P. about 140° / 10mm. and a semi-vitreous solid b.p. about 150° / 10mm. With the object of ascertaining the number of hydroxyl groups in these fractions they were treated with metallic sodium in dry benzene. Solid sodium derivatives were obtained in all three instances, These were filtered off and washed with dry ether as quickly as possible and weighed after drying in a vacuum desiccator. The compounds were decomposed with sulphuric acid and the sodium weighed as Na_2SO_4. The results were

Fraction	WT. of Na derivative	Wt. of Na_2SO_4	% Na.
110-112°	0.1624gm.	0.0478gm.	9.5%
140-142°	0.1690gm.	0.1186gm.	22.7%
150-153°	0.2535gm.	0.1285gm.	16.1%

$C_{10}H_{16}.(ONa)_2$ requires 21.3% ; $C_{10}H_{17}.ONa$ requires 13.0%. The significance of these results has been dealt with elsewhere.

From the middle fraction there was eventually obtained the crystalline glycol in a way described on p. 99 . As oxidation in the traditional method had given only a small yield of this interesting substance the method described on p.108 was applied, hydrolysis being effected with a solution of barium hydroxide in methyl alcohol. The glycol so obtained crystallised in pearly flakes, which effloresced in air. If pressed on porous pot and placed in a vacuum desiccator, these became liquid and then in course of time, solidified to a hard, vitreous solid. If dried slowly, however, it effloresced to a white amorphous powder. It has no definite melting point in the crystalline condition, beginning to melt at 50° and continuing to 56°, but if thoroughly dehydrated it melts at 67·5°. An attempt was made to estimate the water of crystallisation by drying at 100°, but the substance is distinctly volatile at that temperature, and although stable at ordinary temperature it begins to resinify almost immediately at 100°. An approximation was obtained by abstracting the water of crystallisation over sulphuric acid in a vacuum desiccator. The following are the results

		Loss in Wt.
Wt. of crystalline glycol	. 0.5789gm.	
Wt after 5 days in vacuum desiccator .	. 0.4400"	.1389gm.
" 6 " " "	. . 0.4316"	.0084"
" 8 " " "	. . 0.4312"	.0004"
" 9 " " "	. . 0.4308"	.0004"

The discolouration of the sulphuric acid showed that the substance was subliming slightly; in consequence, the loss of weight due to abstraction of water alone can only be approximately estimated. Taking the loss due to water as ·144gm. i.e. 24·8% there would appear to be $3H_2O$ in the crystalline molecule giving 24·1% . Analysis of the hydrated substance gave C= 70·62, H =10·51 ; corresponding to $C_{10}H_{18}O_2$ which requires C = 70·57 , H = 10·68 %. **A solution** of the substance in alcohol was optically inactive. It is unsaturated and can be no other than $\Delta^{8(10)}$ p.Menthen.1:2 diol being represented in its crystalline condition by $C_{10}H_{16}.(OH)_2.3H_2O$.

Repeated attempts to prepare its nitrobenzoate were unsuccessful

On passing dry HBr gas through an ethereal solution of the oil from which the glycol had been removed, keeping the temperature low by surrounding the solution in a freezing mixture, crystals separated. These were unstable but enough was obtained to allow of three crystallisations from ethyl alcohol (the substance is quite unstable in methyl alcohol) The purified compound, which crystallised in pearly flakes melted at 44-45°. An estimation of Br by Carius' method gave 53·5% Br, $C_{10}H_{18}Br_2$ requires 53·64% Br.

Graph showing Changes in the Optical Rotation of Fractions of Oil of Bitter Orange (Limonene Fraction).