

XXVII.—*On Some Constituents of Resin Spirit.*

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THE products of the dry distillation of resin have been made the subject of much investigation by chemists.

As early as 1835, Frémy (*Ann. Chim. Phys.* [2], **59**, 13; *Ann. Chem. Pharm.*, **15**, 284) investigated the products of the distillation of resin, both alone and with quicklime. In the former case he obtained water, turpentine, and a substance boiling above  $250^{\circ}$ , to which he gave the name "*resinein*," and the formula  $C_{20}H_{30}O$ , considering it to be directly derived from resin by the splitting off of a molecule of water. In the latter case he obtained two liquids, one "*resinon*," boiling at  $78^{\circ}$ , and having the formula  $C_{11}H_{18}O$ , the other, "*resineon*," boiling at  $148^{\circ}$ , and corresponding with the formula  $C_{29}H_{46}O$ .

In 1838 Pelletier and Walter (*Ann. Chim. Phys.* [2], **67**, 267; *Pogg. Ann.*, **44**, 81; *Gmelin Org. Chemie*, 4te Auflage, **3**, 690) studied the products obtained from the distillation of resin in the preparation of resin gas for lighting purposes. They described a series of hydrocarbons—

Retinaphtha,  $C_7H_8$ , b. p.  $108^{\circ}$ .

Retinyl,  $C_9H_{12}$ , b. p.  $150^{\circ}$ .

Retinol,  $C_8H_8$ , b. p.  $236-244^{\circ}$ .

Metanaphthalin, m. p.  $67^{\circ}$ , b. p.  $325^{\circ}$ .

Thénard, Robiquet, and Dumas (*Compt. rend.*, 1838, **1**, 460) confirmed these results with the exception of the last hydrocarbon, which they concluded was not isomeric with naphthalene, but had the formula  $C_{28}H_{24}$ , and which they named "retisteren."

Coming down to later times, Schiel (*Annalen*, **115**, 96) investigated the products of the distillation. He separated the products into three divisions. First, the gaseous products, which consist of a mixture of carbonic anhydride, carbon monoxide, ethylene, propylene and diteryl (octané), and are therefore highly inflammable. These gases continue to be given off during the whole time of the distillation. Secondly, the *resin spirit*, a light, mobile, easily inflammable liquid, which boils between  $97^{\circ}$  and  $250^{\circ}$ . Schiel considers this to be a mixture of two substances, viz., "colophonon," boiling at  $97^{\circ}$ , and having the composition  $C_{11}H_{18}O_2$ , and a terpene boiling at  $160^{\circ}$ . And thirdly, *resin oil*, a heavy, viscid, fluorescent liquid boiling above  $250^{\circ}$ , which Schiel considered to be a mixture of several substances.

Couerbe (*J. pr. Chem.*, **18**, 165; *Beilstein's Org. Chemie*, 341) has obtained a pentine from the gas obtained by the dry distillation of resin. It boils at  $50^{\circ}$ .

Resin oil and the so-called naphthalin have been examined by Curie (*Chem. News*, **30**, 189; *Staedel's Jahresber.*, 1874, 453), who has prepared the hydrocarbon by distilling resin with sulphur, and has named it "colophthaline." He describes some of its derivatives which possess, according to him, remarkable properties.

Kelbe (*Ber.*, **13**, 88) has obtained abietic acid in considerable quantities from the resin oil boiling above  $360^{\circ}$ .

From the resin spirit a large number of substances have been separated by various observers. Kelbe (*Ber.*, **13**, 1157) describes two cymenes, boiling at  $170^{\circ}$  to  $178^{\circ}$ , one of which, metaisocymene, is new (*Annalen*, **210**, 1); he also (*Ber.*, **14**, 1240) found an aromatic hydrocarbon,  $C_{11}H_{16}$ , in the fraction boiling  $190$ — $200^{\circ}$ . Isobutyric and methylpropylacetic acids have also been separated by the same chemist (*loc. cit.*, and *Ber.*, **15**, 308) from the low fractions by washing with caustic soda and decomposing the resulting sodium salts.

Renard (*Compt. rend.*, **91**, 419; *Ber.*, **13**, 2000; *Chem. Soc. J.*, Abstr., 1880, 893) obtained a hydrocarbon having the formula  $C_7H_{12}$ , and named by him "heptene." It boils at  $103$ — $104^{\circ}$ . He also describes (*Bull. Soc. Chem.*, **36**, 215; *Ber.*, **14**, 2583) several other hydrocarbons obtainable from resin spirit, whose boiling points range from  $130^{\circ}$  to  $173^{\circ}$ .

Tilden (*Ber.*, **13**, 1604) has identified isobutylaldehyde in the lowest boiling fractions of resin spirit; he also describes a hydrocarbon boiling at  $103$ — $104^{\circ}$ , and a heptane, b. p.  $95$ — $97^{\circ}$ .

Mills ("Destructive Distillation," p. 31) and Anderson (*Chem. News*,

20, 76) have also studied to some extent the products of the distillation of resin.

It has long been observed that the lower fractions of resin spirit yield, on standing for some length of time, a crystalline substance, which appears more readily if the vessels containing the spirit are loosely stoppered. This body has been examined by Tichborne (*Pharm. J. Trans.* [3], **1**, 302), Mills (*loc. cit.*) and Anderson (*loc. cit.*). Dr. Tilden, in his paper mentioned above, announced his intention of further studying this body. Owing, however, to pressure of work in other directions, he was unable to carry out his intention, and kindly gave the substance into my hands for investigation.

### *Preparation of the Substance.*

The crystals are prepared by allowing the lighter portions of resin spirit to stand in large flasks containing about an equal quantity of water. The flasks are tied over with paper, thus allowing the spirit to have free contact with the air. The flasks are repeatedly shaken up, and after standing for some weeks, the watery liquid is separated from the thick oily residue, and gently evaporated on a water-bath. On allowing the concentrated solution to cool, a mass of crystals separates out, which may be purified by repeated crystallisations from water. The substance obtained in this way forms beautiful colourless crystals, often of considerable size.

When the air-dried substance is heated, it melts and gives off a quantity of water, whilst the residue forms, on cooling, a brittle white mass.

### *Analyses of the Crystals.*

The three chemists mentioned above have each obtained different results upon analysis of this substance. Tichborne names the body obtained by crystallisation from water "colophonic hydrate," and assigns to it the formula  $C_{10}H_{22}O_3 \cdot H_2O$ , whilst to the dehydrated substance the name "colophonine" and the formula,  $C_{10}H_{22}O_3$ , are assigned.

The numbers he obtained were as follows:—

For the anhydrous substance—

	I.	II.	$C_{10}H_{22}O_3$ requires
Carbon .....	63.16	62.86	63.15
Hydrogen .....	11.10	11.72	11.58
Oxygen .....	—	—	25.27
			<hr/> 100.00

For the hydrated substance—

	Found.	Theory.
Carbon.....	57·35	57·70
Hydrogen .....	11·32	11·53
Oxygen .....	—	30·77
		<hr/> 100·00

He regards colophonine as isomeric with terpin hydrate, or more probably a homologue of terpin, and derived from terebene, which, however, has since been proved by Armstrong and Tilden (*Ber.*, **12**, 1752) to have no existence, the liquid described as such being a mixture of camphene, cymol, and terpine.

Anderson assigns to the so-called colophonine the formula  $C_7H_{14}O_2$ , having obtained the following numbers upon analysis:—

For the anhydrous body—

	I.	II.	$C_7H_{14}O_2$ requires
Carbon .....	64·43	64·47	64·61
Hydrogen .....	11·09	11·24	10·77
Oxygen .....	—	—	24·62
			<hr/> 100·00

he regards it as being related to terebic acid,  $C_7H_{10}O_4$ . He did not analyse the hydrated crystals.

Mills gives—

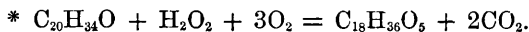
For the anhydrous substance—

Carbon .....	64·69
Hydrogen .....	11·23
Oxygen .....	24·08

From these numbers he obtained the formula  $C_{18}H_{36}O_5$ , which requires—

Carbon .....	65·06
Hydrogen .....	10·84
Oxygen .....	24·10

He regards the crystals as being produced from terpinol by the action of hydrogen peroxide and oxygen, thus:—



For the subjoined analyses, the hydrated substance was prepared by several crystallisations from water, and the crystallised substance was pressed between folds of blotting-paper and then dried by long exposure to the air. The dehydrated body was obtained from this by

\* Tilden *Chem. Soc. J.*, 1878, 247, and 1879, 286) has since shown that terpinol has the formula  $C_{10}H_{17}OH$ .

repeated sublimations and removal of the water given off by bibulous paper. Finally, the substance was distilled three or four times, the last distillate fused, and the fused mass broken up and powdered. Thus obtained, it was a perfectly white powder. Burnt with oxide of copper in a closed tube, finishing in a current of oxygen, it gave the following numbers :—

- I. 0·1860 gram substance gave 0·4394 gram  $\text{CO}_2$ , and 0·1812 gram  $\text{H}_2\text{O}$ .  
 II. 0·1906 gram substance gave 0·4496 gram  $\text{CO}_2$ , and 0·1911 gram  $\text{H}_2\text{O}$ .

	I.	II.	$\text{C}_7\text{H}_{14}\text{O}_2$ requires
Carbon .....	64·43	64·33	64·61
Hydrogen .....	10·81	11·14	10·77
Oxygen .....	—	—	24·62
			<hr/> 100·00

These numbers agree closely with those obtained by Anderson, as will be seen from the subjoined table.

The hydrated crystals gave the following results upon analysis :—

- I. 0·2244 gram substance gave 0·4668 gram  $\text{CO}_2$ , and 0·2168 gram  $\text{H}_2\text{O}$ .  
 II. 0·2336 gram substance gave 0·4850 gram  $\text{CO}_2$ , and 0·2279 gram  $\text{H}_2\text{O}$ .  
 III. 0·1413 gram substance gave 0·2944 gram  $\text{CO}_2$ , and 0·1452 gram  $\text{H}_2\text{O}$ .

	I.	II.	III.	$\text{C}_7\text{H}_{14}\text{O}_2 \cdot \text{H}_2\text{O}$ requires
Carbon.....	56·73	56·62	56·82	56·75
Hydrogen....	10·75	10·82	11·42	10·81
Oxygen ....	—	—	—	32·43
				<hr/> 99·99

These results point to the formula  $\text{C}_7\text{H}_{14}\text{O}_2$  for the anhydrous body, and  $\text{C}_7\text{H}_{14}\text{O}_2 \cdot \text{H}_2\text{O}$  for the hydrated crystals. The means of the analyses obtained by the different observers are tabulated below. It will be seen that they do not differ very considerably from each other.

	Tichborne.	Mills.	Anderson.	Morris.
Hydrated crystals, C....	57·35	—	—	56·72
„ „ H....	11·32	—	—	10·99
Anhydrous body, C....	63·01	64·69	64·65	64·38
„ „ H....	11·41	11·23	11·16	10·95

The vapour-density of the anhydrous substance was taken by Hofmann's method, and gave the following result :—

Weight of substance taken .....	0.0682 = P
Observed volume of vapour .....	50.5 c.c. = V
Height of mercury column above level in trough .....	428 mm. = H
Height of barometer .....	735 mm. = B
Boiling point of aniline .....	190° C. = <i>t</i>
Temperature of room .....	16.5 C. = <i>t'</i>
Tension of mercury vapour at 190° C .....	15 mm. = T
Mercury column corrected to <i>t'</i> .....	= H'
Vapour-density required .....	= D

$$H' = H [1 - 0.00018 (t - t')],$$

$$H' = 428 [1 - 0.00018(190 - 16.5)],$$

$$H' = 414.6 \text{ mm.}$$

$$D = \frac{P \cdot (1 + 0.00367t) \cdot 760 \cdot 14.42}{0.0012932 \cdot V(B - H' - T)} \text{ (hydrogen = 1),}$$

$$D = \frac{0.0682 (1 + 0.00367 \cdot 190) \cdot 760 \cdot 14.42}{0.0012932 \cdot 50.5 (735 - 414.6 - 15)} = 63.6.$$

	Found.	C <sub>7</sub> H <sub>14</sub> O <sub>2</sub> calculated.
Vapour-density .....	63.6	65

### *Properties of the Crystals.*

This body is readily soluble in water, alcohol, ether, benzol, &c., and crystallises from its solutions in brilliant colourless prisms. When heated, it begins to sublime about 100° C., and melts at about 106°, giving off water. When the whole of the water is removed, the dehydrated substance melts at 89.5°, and boils without decomposition at 195.6° (corr.). The solution in water is perfectly neutral to test-paper, and gives no precipitate with basic lead acetate or ammoniacal silver nitrate. When the crystals are treated with sulphuric or hydrochloric acid, and warmed, a series of colours is observed in the order of yellow, red, green, deep blue; and on adding this liquid to alcohol, a magnificent green colour is communicated to it. Phosphoric, tartaric, and citric acids give the same reactions. Excess of hydrochloric acid in the cold, gives, after standing, a fine rose colour with alcohol. A very small quantity of the substance gives these reactions, so that it constitutes a delicate test for this substance, and also for the hydrocarbon to be described further on.

The hydrated crystals cannot be completely deprived of their water of crystallisation over sulphuric acid in a vacuum. A portion appears to be given off, but the substance itself is volatile, and the sulphuric acid gradually becomes green, in consequence of the reaction above mentioned.

*Formation of the Crystals.*

The boiling point of the fraction from which this body is obtainable in the largest quantity is variously stated. Anderson gives 125—150°, Mills 154—163°, whilst I find that the fraction boiling between 100—105° furnishes by far the largest supply, although crystals separate out from all the fractions ranging from 94—150°, after they have been standing for some time, either in loosely stoppered bottles or bottles partially filled with air.

According to Anderson (*loc. cit.*) resin spirit contains a hydrocarbon boiling at 70—80°, which he considers to be a heptylene. It gave the following percentage on analysis :—

	Found.	Calculated $C_7H_{14}$ .
Carbon .....	84.62	85.7
Hydrogen.....	13.71	14.3

Vapour-density determination gave—

	Found.	Calculated $C_7H_{14}$ .
Vapour-density....	3.257 (air = 1)	3.386

He considers the lowness of the numbers to be due to the presence of oxygen.

Renard (*Compt. rend.*, **91**, 419) describes a hydrocarbon obtained from resin spirit, which he calls “heptene.” It boils at 103—106°, and gave the following numbers :—

	I.	II.	$C_7H_{12}$ requires
Carbon .....	87.2	87.3	87.5
Hydrogen.....	12.7	12.7	12.5

The vapour-density determination gave—

	Found.	$C_7H_{12}$ requires
Vapour-density....	3.22 (air = 1)	3.31

It has a specific gravity of 0.8031 at 20°; it is colourless, mobile, has a characteristic odour, and is soluble in alcohol and ether. It absorbs oxygen very readily, and is without action upon an ammoniacal solution of copper chloride or silver nitrate.

It gives with bromine two compounds,  $C_7H_6Br_6$  and  $C_7H_{12}Br_2$ . The formula of the latter was obtained by observing the amount of bromine, which a known quantity of the hydrocarbon decolorised, when the two were brought together in ethereal solution.

Oxidised with nitric acid of 1.15 sp. gr., it yields, according to Renard, carbonic anhydride, carbon monoxide, acetic, formic, oxalic, and succinic acids.

Treated with a mixture of ordinary and fuming sulphuric acid, it yields a hydrocarbon, "diheptine,"  $C_{14}H_{24}$ , polymeric with the first, boiling at  $235-250^\circ$ , and giving on analysis :—

		$C_{14}H_{24}$ requires
Carbon .....	86.9	87.5
Hydrogen .....	12.2	12.5

This hydrocarbon is very oxidisable, and quickly resinifies on exposure to the air. It absorbs oxygen eight or ten times as rapidly as heptene.

Tilden (*loc. cit.*) describes a liquid from the same source, boiling steadily at  $103-104^\circ$ , which gave on analysis :—

	I.	II.	$C_7H_{12}$ requires
Carbon .....	86.90	87.09	87.5
Hydrogen .....	12.39	12.57	12.5

but he considered it to be a mixture of hydrocarbons. It gives on treatment with sulphuric acid, a hydrocarbon boiling at  $245-247^\circ$ , and containing—

	Found.	$(C_7H_{14})_n$ requires	$(C_5H_8)_n$ requires
Carbon .....	87.36	87.5	88.2
Hydrogen .....	12.09	12.5	11.8

This Dr. Tilden considered at the time to be a polymerised terpene; but, as will be seen from the calculated numbers, it agrees almost exactly with the percentage required for diheptene.

A vapour-density determination was made of the above-mentioned hydrocarbon by Hofmann's method. The numbers obtained were :—

Weight of substance taken .....	0.0470	= P
Observed volume of vapour .....	31.2 c.c.	= V
Height of mercury column above level in trough .....	612.5 mm.	= H
Height of barometer .....	754 mm.	= B
Boiling point of aniline .....	$190^\circ$ C.	= $t$
Temperature of room .....	$15^\circ$ C.	= $t'$
Tension of mercury vapour at $190^\circ$ C. ..	15 mm.	= T
Mercury column corrected to $t'$ .....		= $H'$
Density required .....		= D

$$H' = H [1 - 0.00018(t - t')],$$

$$H' = 612.5 [1 - 0.00018(190 - 15)],$$

$$H' = 593.4 \text{ mm.}$$

$$D = \frac{P \cdot (1 + 0.00367t) \cdot 760 \cdot 14.42}{0.001293 \cdot V \cdot (B - H' - T)} \text{ (hydrogen = 1).}$$



$$D = \frac{0.0470 \cdot (1 + 0.00367 \cdot 190) \cdot 760 \cdot 14.42}{0.0012932 \cdot 31.2(754 - 593.4 - 15)}.$$

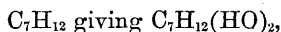
$$D = 94.23.$$

	Found.	(C <sub>7</sub> H <sub>12</sub> ) <sub>2</sub> .	(C <sub>8</sub> H <sub>8</sub> ) <sub>4</sub> .
Vapour-density....	94.23	96	136

The result agrees closely with that required for diheptene. The hydrocarbon used, for which I am indebted to Dr. Tilden, was boiled with sodium for some hours, and finally distilled from that metal.

From these results there can be no doubt that the hydrocarbon contained in resin spirit, and boiling at 103—104°, is a heptene.

The anhydrous substance may then be regarded as derived from this hydrocarbon by the addition of 2 semi-mols. of hydroxyl—



and the hydrated crystals as being the hydrate of this body with 1 mol. of water,  $C_7H_{12}(HO)_2 \cdot H_2O$ .

Both the hydrocarbons mentioned above give, even immediately after distillation from sodium, the series of colours referred to in connection with the crystals.

### *Oxidation of Heptene.*

*Nitric Acid.*—When heptene is added to nitric acid of 1.3 sp. gr., a violent action takes place, torrents of red fumes are evolved, and the liquid shows the characteristic green colour. Upon boiling this disappears, carbonic anhydride is evolved, and, after a time, a crystalline sublimate begins to form upon the sides and neck of the flask. When the action is complete, the sublimate is washed back into the acid liquid, and the whole distilled.

The crystalline body then distils over with the volatile acids. It was collected, washed, and dried. It is soluble in alcohol, and crystallises from it in shining plates. It appears to be a *dinitro-heptylene*. The purified substance gave the following numbers on analysis:—

- I. 0.1576 gram substance gave 0.2579 gram CO<sub>2</sub>, and 0.0925 gram H<sub>2</sub>O.
- II. 0.1650 gram substance gave 21.7 c.c. of nitrogen at 754.2 mm. Bar., and 13° C.

	I.	II.	C <sub>7</sub> H <sub>12</sub> (NO <sub>2</sub> ) <sub>2</sub> requires
Carbon .....	44.62	—	44.68
Hydrogen .....	6.52	—	6.38
Nitrogen .....	—	15.44	14.89

Dinitro-heptylene is easily soluble in alcohol, ether, and benzol,

insoluble in water, and not decomposed on boiling with alkalis. It is volatile in a current of steam. It melts at  $182^{\circ}$ , and sublimes a little above that temperature, undergoing partial decomposition. I am at present endeavouring to obtain this substance in larger quantities by a different method.

The distillate containing the volatile acids was neutralised with sodium carbonate, evaporated to a small bulk, and fractionally precipitated with silver nitrate. The silver salts gave the following numbers:—

1st precipitate 0.1160 gram gave 0.0646 gram Ag.

2nd „ 0.0480 „ 0.0276 „

	I.	II.	Silver butyrate requires
Silver .....	55.68	57.50	55.38

The liquid after precipitation contained acetic and formic acids.

On evaporating off the remainder of the nitric acid on a water-bath, a crystalline acid remained. This was repeatedly evaporated with water to expel the whole of the nitric acid, and then crystallised from water. It was slightly discoloured, and gave the following numbers on analysis:—

0.1950 gram acid gave 0.2862 gram  $\text{CO}_2$  and 0.0972 gram  $\text{H}_2\text{O}$ .

		$\text{C}_2\text{H}_4(\text{COOH})_2$ requires
Carbon .....	40.02	40.68
Hydrogen .....	5.53	5.08
Oxygen .....	54.45 (by diff.)	54.23

The acid gave all the reactions for succinic acid. The barium salt, which was slightly discoloured, was prepared by mixing a solution of the acid, neutralised with ammonia, with barium chloride, and then precipitating with alcohol. The air-dried salt gave the following results on analysis:—

I. 0.2511 gram salt gave 0.2189 gram  $\text{BaSO}_4$ .

II. 0.7001 gram salt lost 0.0507 on drying at  $100^{\circ}\text{C}$ .

	I.	II.	Calculated for $\text{C}_2\text{H}_4(\text{COO})_2\text{Ba}, \text{H}_2\text{O}$ .
Barium .....	51.24	—	50.55
Water .....	—	7.24	6.64

The barium salt dried at  $100^{\circ}$  gave—

0.4856 gram  $\text{BaSO}_4$  from 0.5286 gram salt.

	Found.	$\text{C}_2\text{H}_4(\text{COO})_2\text{Ba}$ .
Barium .....	54.01	54.15

The products, therefore, of the oxidation of heptene with nitric acid

are: carbonic anhydride, formic, acetic, butyric, and succinic acids. There is also formed in small quantity dinitroheptylene.

*Potassium Bichromate*.—Heptene, oxidised with a 10 per cent. solution of bichromate, is completely converted into carbonic anhydride and acetic acid.

The acid distillate, after oxidation, neutralised with barium carbonate, gave on evaporation a crystalline barium salt. This salt, purified by recrystallisation at a low temperature, gave the following numbers:—

I. 0.6625 gram salt gave 0.5026 gram  $\text{BaSO}_4$ .

II. 0.8416 gram salt lost 0.1398 gram  $\text{H}_2\text{O}$ .

III. 0.7018 gram dry salt gave 0.6414 gram  $\text{BaSO}_4$ .

	Found.	Calculated for $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ .
I. Barium .....	44.60	44.20
II. Water .....	16.61	17.40
III. Barium .....	53.70	$\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ 53.72

*Potassium Permanganate*.—Heptene is readily oxidised by potassium permanganate solution, yielding an acid which has not yet been examined. No carbonate is formed.

#### *Oxidation of the Crystals.*

The crystalline substance oxidised with nitric acid of 1.3 sp. gr. yields the same acids, with the exception of formic, as the hydrocarbon.

The volatile acids, treated in the same way as the acids in the latter oxidation, gave silver salts, giving the following numbers:—

1st precipitate 0.1042 gram salt gave 0.0575 gram silver.

2nd „ 0.1092 „ 0.0624 „

	I.	II.	$\text{AgC}_4\text{H}_7\text{O}_2$ requires
Silver .....	55.18	57.14	55.38

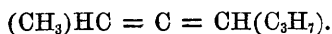
The non-volatile acid agrees in all its reactions with that obtainable from the hydrocarbon.

0.4570 gram of the barium salt gave 0.3915 gram  $\text{BaSO}_4$ .

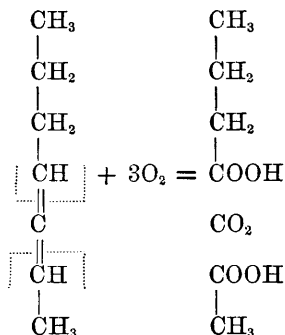
	Found.	$\text{C}_2\text{H}_4(\text{COO})_2 \cdot \text{Ba} \cdot \text{H}_2\text{O}$ .
Barium .....	50.76	50.55

#### *Probable Constitution of Heptene and its Glycol.*

From the products of oxidation of the hydrocarbon, it is probably methylpropylallylene—

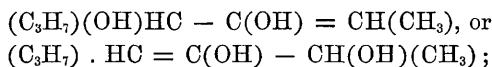


this would probably split up on oxidation, thus:—



yielding butyric and acetic acids and carbon dioxide. The succinic and formic acids may result from a secondary oxidation or from the oxidation of the butyric acid (Sigel and Belli, *Annalen*, **180**, 207).

The dehydrated crystals would then have the constitution—



either of these would yield butyric and acetic acids on oxidation. It would then be methylpropylallyleneglycol.

*Action of Acetic Anhydride upon Methylpropylallyleneglycol.*

The substance was heated with twice its weight of acetic anhydride upon a water-bath. After a short time the liquid became dark coloured, and deepened in colour on distilling off the excess of acetic anhydride. The residue was then evaporated on a water-bath. A dark-coloured syrup was left, which on standing deposited a quantity of crystalline matter. This was drained on a filter-pump, dried between blotting-paper, and crystallised from alcohol. The acetate thus obtained crystallises in square plates, melting at  $68.5^\circ$ . It is very soluble in alcohol, ether, and benzol, so soluble that it was found impossible to free it, by this means, from a slight discoloration.

Warming the alcoholic solution with animal charcoal was equally unsuccessful. The acetic acid was determined by boiling a weighed quantity with caustic potash, acidifying with sulphuric acid, distilling off the acetic acid liberated, and neutralising the distillate with barium carbonate. The barium acetate was filtered off, and the solution evaporated to dryness in a weighed dish and dried at  $110^\circ$ .

Treated in this way—

0.3311 gram substance gave 0.4014 barium acetate.

	Found.	$C_7H_{12}(C_2H_3O_2)_2$ requires
$(C_2H_3O_2)$ .....	56.08	55.01

The compound obtained from the crystals and acetic anhydride is therefore the diacetate.

*Action of Bromine.*

When bromine is added in slight excess to an aqueous solution of the crystals, a heavy yellow oil separates out. This oil is soluble in alcohol, benzene, and ether. A bromine determination of the dried oil gave the following result:—

0.3052 gram substance gave 0.5198 gram silver bromide and 0.0178 metallic silver.

	Found.	$C_7H_{12}Br_4$ requires
Bromine.....	76.70	76.92

The watery liquid from which the oil has been separated becomes almost solid, upon standing in contact with air, from separation of a black substance, which appears to be identical with that obtained by the action of sulphuric acid on the hydrocarbon or crystals.

*Action of Hydriodic Acid on the Hydrocarbon.*

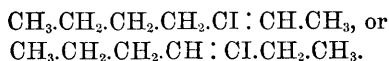
When gaseous hydriodic acid is passed into heptene it is rapidly absorbed, the liquid becomes dark coloured, and if the temperature is allowed to rise, the characteristic green colour is produced. The gas was passed into the hydrocarbon until the liquid was saturated, the temperature being kept down. The dark-coloured iodide was separated from a small quantity of resinous matter formed, washed with a little dilute caustic potash to remove free hydriodic acid and iodide, and dried with calcium chloride.

The iodide was, however, still dark coloured, resembling a solution of iodine in potassium iodide, and slowly decomposed on standing. It boiled between  $140-150^\circ$ , decomposing, and giving off large quantities of hydriodic acid. An iodine determination by Carius' method gave the following numbers:—

0.1854 substance gave 0.2049 AgI.

	Found.	$C_7H_{13}I$ requires
Iodine.....	59.76	56.60

It is therefore a moniodide, the high percentage found being due to the spontaneous decomposition of the substance. Assuming the hydrocarbon to be methylpropylallylene, the formula of the iodide would be—



Experiments were made in order to prepare the corresponding alcohol, but without success.

Portions were treated with potassium acetate and caustic potash, lead hydrate and water, as recommended by Flavitzky (*Annalen*, **175**, 380), and moist silver oxide, but in each case a hydrocarbon was obtained boiling at 103—104°, and possessing all the properties of the original hydrocarbon.

A portion of the regenerated hydrocarbon was set aside with water, as in the preparation of the crystals; and, after some days, the watery liquid contained a considerable quantity of the crystalline body.

As already mentioned, both the hydrocarbon and the crystals give with acids and other reagents, such as bromine, chlorine, &c., a black substance soluble in spirit, producing a fine green colour. This body is at present under investigation, together with some other reactions of the bodies above mentioned.

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