

VII. *On the Normal Paraffins.* By C. SCHORLEMMER, F.R.S.

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IN the year 1858 BERTHOLET proved that the compound $\text{CH}_3 \text{Cl}$, obtained by the action of chlorine upon marsh-gas, was identical with methyl chloride, by converting it into methyl alcohol and other methyl compounds. Since that time the researches of PELOUZE and CAHOURS, as well as my own, have shown that this method is a general one, and that by means of it the corresponding alcohol may be prepared from any paraffin.

On oxidizing some of the alcohols obtained by this method, acids were formed containing the same number of carbon atoms in the molecule as the alcohols themselves contained, from which it would appear that these alcohols were primary alcohols.

PELOUZE and CAHOURS, however, stated that the octyl alcohol which was obtained from octane contained in petroleum was identical with the so-called capryl alcohol prepared from castor-oil, and CHAPMAN afterwards came to the same conclusion. At that time it was believed that capryl alcohol was a primary alcohol. However, by the study of its oxidation products I found this not to be the case, but that this alcohol belongs to the group of secondary alcohols, being methyl-hexyl carbinol*. It was therefore necessary to repeat the experiments of PELOUZE and CAHOURS and CHAPMAN, and to study carefully the oxidation products of the alcohol from petroleum, which none of these chemists had done. The result of my investigation was that this alcohol is a mixture of methyl-hexyl carbinol with a primary octyl alcohol†.

This observation made it highly probable that, by acting with chlorine upon the paraffins, primary and secondary chlorides are formed at the same time; and the more so, as I had formerly found an acetone amongst the oxidation products of the amyl alcohol from petroleum, the origin of which I was then at a loss to explain‡. As I have already stated in a preliminary note, further experiments with hexane fully confirmed the correctness of my supposition.

The reasons why, in my former researches, I overlooked the secondary compounds are the following:—

The mixture from which the chlorides had to be isolated contained, besides large quantities of unattacked hydrocarbon, also higher chlorinated products. The difference between the boiling-points of the two chlorides is about 10° , but by far the greatest portion distils within these limits at a nearly constant temperature; and as by fractional distillation the boiling-point becomes yet more constant, and the quantity of liquid distilling at this temperature increases, I believed I had obtained a pure compound, and considered the smaller quantities of liquids boiling a little above and below the constant

* Proc. Roy. Soc. vol. xvi. p. 376.

† Ibid. vol. xviii. p. 25.

‡ Ibid. vol. xvi. p. 372.

point to consist of mixtures of the chloride with the paraffin, or with higher chlorinated products.

To convert the chlorides into the alcohols, they were first heated with potassium acetate; during this operation a large quantity of the secondary chloride splits up into hydrochloric acid and an olefine, from which the acetic ethers formed had again to be separated by fractional distillation. From the highest boiling fraction, which of course consisted chiefly of the primary acetate, the alcohol was then prepared; but the quantity obtained was so small, that the acid formed by oxidizing it could not be isolated, and its existence was only proved by analyzing the silver salt, in the preparation of which the small quantity of the acetone remained in aqueous solution and was thus overlooked.

As soon as I had ascertained that by acting with chlorine upon the paraffins a mixture of primary and secondary chlorides is formed, the problem next to be solved was under what conditions the one or the other is formed.

In order to obtain decisive results, it was first of all required to work with large quantities of a hydrocarbon; and I chose for my first experiments the *hexyl hydride* or *hexane*, C_6H_{14} , from petroleum, a hydrocarbon which can be obtained most easily in a sufficient quantity. The hexane was treated with chlorine under the following conditions:—

- (1) Dry chlorine was passed into the well-cooled hydrocarbon in diffused daylight.
- (2) It was acted upon in the cold by chlorine in presence of iodine.
- (3) Chlorine was passed into the vapour of the boiling hydrocarbon.
- (4) Chlorine was passed into the vapour in the presence of iodine.

The result was that in all four cases, as first product, a mixture of primary and secondary hexyl chlorides was formed. Further, it was found that when chlorine acts on the liquid hydrocarbon, or when iodine is present, always large quantities of higher chlorinated products are formed, but that by passing chlorine to the vapour, the formation of these bodies can be almost completely avoided. In investigating the other paraffins, to be described further on, I always used the latter method.

The apparatus employed consisted of a large flask, which, by means of a cork, was connected on one side with the chlorine apparatus by a tube reaching to the lower end of the neck, and on the other side with a reversed LIEBIG's condenser, the upper end of which was further connected with absorption-bottles containing caustic soda solution, and in which the hydrocarbon which was carried away by the current of hydrochloric acid was condensed. On passing a moderately strong current of dry chlorine into the vapour of the gently boiling hydrocarbon, the colour of the chlorine disappears instantaneously, and the chloride formed is seen to flow back in oily streaks on the side of the vessel. The operation was interrupted in the evening, the hydrocarbon not acted upon distilled off, and treated repeatedly in the same way until a sufficient quantity of the chlorides had been formed. The latter were then heated with the required quantity of potassium acetate, and an equal volume of glacial acetic acid in sealed tubes to 190° to

200° for two or three hours by which they were completely decomposed. On diluting the contents of the tubes with water, a light layer, a mixture of olefines and acetates, separated out, from which, after drying, the acetates were isolated by fractional distillation, and then decomposed by an alcoholic solution of caustic potash. The alcohols thus obtained were repeatedly washed with small quantities of water and dried, first with fused potassium carbonate, and finally with anhydrous baryta.

Whilst neither a mixture of the two chlorides nor of the acetic ethers can be separated even approximately into its constituents, it is, however, easy to obtain from the mixed alcohols two liquids, each having a nearly constant boiling-point. But although apparently a definite separation has thus been effected, the bodies obtained in this manner are far from being pure compounds. This might have been expected *à priori*, as the difference between the boiling-points of the two alcohols is only about 10°. The products of oxidation showed that the lower boiling liquid consisted principally of the secondary alcohol, but still mixed with some of the primary; whilst in the higher boiling liquid, besides a large quantity of primary alcohol, also some secondary was contained.

In order to oxidize the alcohols, I used, as in my former researches, a solution consisting of two parts of potassium dichromate, three parts of sulphuric acid, and ten parts of water, which was added gradually to the alcohols until the brownish colour of the liquid indicated an excess of chromic acid, care being taken at the same time to keep the liquids as cold as possible. After standing for some time, and being repeatedly shaken, the liquid was diluted with water and distilled, when the acetone formed passed over with the first portion. The residue was again distilled with water, and this operation repeated as long as the distillate exhibited an acid reaction. The aqueous distillates were neutralized with sodium carbonate, the acetone which dissolved in them separated by distillation, and the solution of the sodium salts evaporated to dryness. By adding dilute sulphuric acid to the residue, the acid was liberated and dried with phosphorus pentoxide.

*Normal Amyl Hydride or Pentane**, C_5H_{12} .

This hydrocarbon is a mobile colourless liquid, boiling at 37° to 39°, which I first discovered in the light oils from candle tar†; it is also found in boghead tar, and in large quantities in Pennsylvania petroleum. According to PELOUZE and CAHOUS, the amyl hydride from petroleum boils at 30°‡, whilst WARREN has found that it contains two isomerides, C_5H_{12} , one boiling at 30°·2 and the other at 37°§. My last researches agree with WARREN'S statement. I have formerly stated that the amyl hydride from petroleum boiled at 35°||; but this body, as well as the derivatives which I prepared from it, are, as I have now found, only mixtures. The petroleum which I used for this research

* HOFMANN calls this hydrocarbon *quintane* and its derivatives *quintyl compounds*. I prefer the names *pentane* and *pentyl*, as corresponding with hexyl and heptyl, which terms are now in general use.

† Journ. Chem. Soc. vol. xv. p. 419.

‡ Ann. Chim. Phys. [4] vol. i. p. 5.

§ Chem. News, vol. xiii. p. 74, from Mem. Amer. Academy.

|| Proc. Roy. Soc. vol. xv. p. 131.

contained but small quantities of the hydrocarbon boiling at 30° ; by long-continued and carefully conducted fractional distillation I succeeded in obtaining about 800 cub. centims. of pure pentane, boiling constantly at 37° to 39° , the boiling-point of which was not altered by further distillations.

The mixture of pentyl chloride obtained by the method described above boiled between 95° and 110° , the principal fraction distilling at 100° to 102° . On decomposing these chlorides with potassium acetate, a mixture of pentene boiling at 39° to 40° , and of the acetic ethers boiling at 135° to 145° , was formed. The latter were converted into the alcohols, which by fractional distillation could be separated into two portions, one boiling at 120° to 122° , and the other at 134° to 137° . The products of oxidation of the alcohols were found to consist of *methyl-propyl ketone*, $\left. \begin{matrix} \text{C H}_3 \\ \text{C}_3 \text{ H}_7 \end{matrix} \right\} \text{CO}$, and *normal valerianic* or *pentylic acid*.

Methyl-propyl ketone is a colourless liquid boiling at 102° to 105° , having the same boiling-point as the ketone obtained by the distillation of a mixture of calcium acetate and butyrate, and that formed by oxidation of isoamylic alcohol. It combines with the bisulphites of the alkali-metals, and yields by further oxidation acetic and propionic acids. The aqueous distillate containing these acids was neutralized with sodium carbonate, the solution evaporated, and from the residue the acids liberated by successive distillations with insufficient quantities of sulphuric acid in four fractions, from which, by boiling with silver carbonate, the silver salts were prepared, which were analyzed.

Calculated for silver propionate	59.67 per cent.
First fraction, small, white needles, 0.335 gave 0.199 Ag=	59.6 per cent.
Second fraction was lost.	
Third fraction, indistinct needles, 0.481 gave 0.307 Ag=	63.69 per cent.
Fourth fraction, shining flat needles, 0.2095 gave 0.135 Ag=	64.5 per cent.
Calculated for silver acetate	64.67 per cent.

The acid derived from the primary pentyl alcohol contained small quantities of acetic and propionic acids, which were easily removed by distillation. The pure acid boils at 184° to 187° , and smells very much like common butyric acid; these are the properties of normal valerianic acid*, or, as it might conveniently be called, *pentylic acid*.

The following salts were prepared and analyzed:—

Silver pentylate, $\text{C}_5 \text{ H}_9 \text{ O}_2 \text{ Ag}$, is a white precipitate, which crystallizes from a boiling solution in woolly needles.

0.834 dried at 100° gave 0.4304 Ag.

Calculated for $\text{C}_5 \text{ H}_9 \text{ O}_2 \text{ Ag}$.
51.67 per cent.

Found.
51.6 per cent.

Barium pentylate, $(\text{C}_5 \text{ H}_9 \text{ O}_2)_2 \text{ Ba} + 1\frac{1}{2} \text{ H}_2 \text{ O}$, obtained by neutralizing the aqueous

* Ann. Chem. Pharm. vol. clix. p. 58.

solution of the acid with barium carbonate, crystallizes from a hot concentrated solution in pearly scales.

0.5967 lost, on drying at 180° , 0.040 of water, or 6.7 per cent., the formula requiring 7.4 per cent. H_2O .

On igniting the dry residue, 0.3265 Ba CO_3 were left behind, corresponding to 40.8 Ba, the calculated quantity being 40.4 per cent.

The salt obtained by spontaneous evaporation of the solution is, according to LIEBEN and ROSSI, anhydrous. I have therefore, after the publication of LIEBEN's and ROSSI's complete paper on normal valerianic acid, prepared this salt again; by spontaneous evaporation it was obtained in small plates and needles, which, after being dried in the air at the common temperature, lost at 180° , 2.6 per cent. of water, corresponding to $\frac{1}{2} \text{H}_2\text{O}$.

0.316 of the salt, dried at 180° , gave 0.1832 Ba CO_3 , corresponding to 40.3 per cent. Ba.

LIEBEN and ROSSI prepared their salt in the dry climate of Turin, whilst I worked in the damp air of Manchester, which may account for the differences.

Calcium pentylate, $(\text{C}_5 \text{H}_9 \text{O}_2)_2 \text{Ca} + 1\frac{1}{2} \text{H}_2\text{O}$, obtained by neutralizing the acid with milk of lime, crystallizes on spontaneous evaporation in shining leaflets.

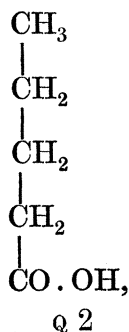
0.2958 lost, at 180° , 0.0293 H_2O , or 9.9 per cent., the amount required for the above formula being 10 per cent.

The dry residue left on ignition 0.111 Ca CO_3 , corresponding to 16.7 per cent. Ca, the calculated percentage being 16.5.

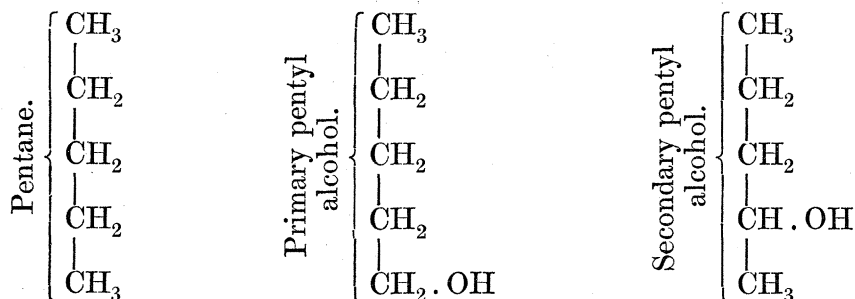
LIEBEN's salt contained only 1 vol. of water; but all other properties of these salts, which LIEBEN has described so very minutely, agree perfectly. From the cold saturated solution shining laminæ separate on heating, the greater portion of which dissolve again on cooling; on the other hand, a solution saturated at 100° gives on cooling to 70° a crystalline precipitate, which on further cooling nearly completely redissolves. I have repeated these experiments several times, following exactly LIEBEN's instructions, and with exactly the same results.

Besides pentylic acid and methyl-propyl ketone, I also obtained a small quantity of a high boiling liquid, having a pleasant smell like apples, which principally consisted of pentyl pentylate, as on decomposing it with caustic potash, pentyl alcohol, boiling at 134° to 137° , and pentylic acid were formed.

As there can be no doubt that LIEBEN and ROSSI's normal valerianic acid has the following constitution,



it follows that the carbon atoms are grouped together in the same way in the pentane, which, therefore, belongs to that group of the paraffins which I have called "normal paraffins;" and the constitution of it and those of the alcohols derived from it are expressed by the following formulæ:—



The primary pentyl alcohol from pentane is identical with LIEBEN and ROSSI's normal amyl alcohol; and the secondary alcohol is methyl-propyl carbinol, a compound obtained by FRIEDEL by the action of nascent hydrogen on methyl-propyl carbinol. The isoamyl alcohol obtained by WURTZ from isoamylenes or ethyl allyl, appears to have the same constitution.

Normal Hexyl Hydride, or Hexane, C₆H₁₄.

This hydrocarbon was discovered by PELOUZE and CAHOURS in American petroleum. It is also found in cannel and boghead tar, and other coal tars. According to WARREN, petroleum contains, besides the hexane boiling at 68°, an isomeric hydrocarbon, which boils at 61°·3*. In the petroleum which I used this latter body was not present, the fractions between 40° and 68° being quite insignificant, and diminishing on each further distillation.

The monochlorides obtained from hexane boil between 120° and 130°, by far the largest portion distilling nearly constantly at 125° to 126°, as PELOUZE and CAHOURS have already observed. On acting upon them with potassium acetate, hexene boiling at 69° to 70° is obtained, and a mixture of the two hexyl acetates, which boil at 158° to 170°, and not, as PELOUZE and CAHOURS state, at 145°. The alcohols obtained from the acetic ethers were readily separated by fractional distillation into two portions, one boiling at 140° to 141°, and the other between 150° and 155°. As I have already stated, this separation of the alcohols is only very incomplete. I tried to obtain the pure alcohols by preparing the iodides and transforming those again in the alcohols. The iodide obtained from the portion boiling at 140° gave an iodide, the chief portion of which boiled, after fractional distillation, at 164° to 169°. On heating it with potassium acetate and glacial acetic acid to 100°, nearly half of it was decomposed into hexene and hydriodic acid, whilst the remaining portion was converted into an acetate boiling at 155° to 159°, from which the alcohol was regenerated, but could not be further examined, as it was lost.

* Chem. News, vol. xiii. p. 74, from Memoirs Amer. Academy.

The iodide prepared from the alcohol boiling at 150° to 155° was subjected to fractional distillation; the largest portion of it boiled constantly at 170° to 171°. On decomposing it with potassium acetate, $\frac{1}{6}$ was converted into hexene and $\frac{5}{6}$ into hexyl acetate, which boiled at 160° to 164°. The alcohol prepared from this acetate boiled now at 149° to 152°, and yielded on oxidation caproic acid, besides a not inconsiderable quantity of methyl-butyl ketone, from which it follows that it was still a mixture of primary and secondary hexyl alcohol.

The difference between the boiling-points of the primary and secondary iodide is too small to effect in this way a separation of the alcohols.

Methyl-butyl ketone, $\begin{matrix} \text{C H}_3 \\ \text{C}_4 \text{H}_9 \end{matrix} \bigg\} \text{CO}$, was obtained, as well as caproic acid, by oxidizing the mixture of the two hexyl alcohols, as described above. It is a colourless liquid with a pleasant smell, and boiling at 126° to 128°, which forms crystalline compounds with the bisulphites of the alkaline metals. It exhibits, therefore, all the properties of the acetone which ERLÉNMEYER and WANKLYN obtained by oxidizing methyl-butyl carbinol on the secondary hexyl alcohol obtained from mannite. On further oxidation it yields, like the latter compound, acetic and butyric acids, which were converted into the silver salts.

Calculated for silver butyrate				55.38 per cent.
1st fraction, crystalline crusts,	0.792	gave 0.44	Ag=	55.56 per cent.
2nd „ small needles,	0.2758	„ 0.153	Ag=	55.47 per cent.
3rd „ small needles,	0.3695	„ 0.2335	Ag=	63.18 per cent.
4th „ shining, flat needles,	0.966	„ 0.646	Ag=	64.85 per cent.
Calculated for silver acetate				64.67 per cent.

In order to throw light on the constitution of hexane, it was necessary to investigate closely the butyric acid obtained from it. To isolate this acid, the aqueous distillates obtained in the oxidation of the acetone were repeatedly distilled, when the butyric acid came over with the first portions, whilst the greatest part of the acetic acid was left behind. The aqueous solution of the butyric acid thus obtained was neutralized with milk of lime and evaporated on the water-bath. The butyrate separated as a crystalline scum on the surface, which was not wetted by water. The cold saturated solution of this salt, contained in a sealed tube, was heated to 70°–80°, when shining laminae separated, which, on cooling, slowly but completely redissolved. This experiment was more than ten times repeated, always with the same results. The calcium salt possesses therefore all the characteristic properties of normal calcium butyrate.

The primary alcohol from hexane yielded as the product of its oxidation caproic acid, boiling at 200° to 205°. The silver salt is a white precipitate, which from a hot solution crystallizes in small needles.

(1) 0.5029 of this salt gave 0.2444 Ag.

(2) On evaporating the mother-liquor a second crop was obtained, 0.166 of which gave 0.0800 Ag.

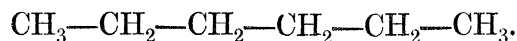
Calculated for $C_6H_{11}O_2Ag$. 48.43 per cent. Ag	Found.	
	I.	II.
	48.59	48.19

The calcium salt crystallizes from a hot concentrated solution in shining scales; by spontaneous evaporation it is obtained in ramified needles.

The most characteristic salt of this acid is the barium salt, which could not be obtained in the crystalline state, but which on evaporating an aqueous or alcoholic solution at a higher or at the common temperature, is always obtained as an amorphous, gum-like mass.

As the caproic acids of different origin have been so far very little studied, I have not investigated the salts of my acid more fully.

The oxidation products of the secondary hexyl alcohol or methyl-butyl carbinol, viz. *acetic acid* and *normal butyric acid*, are quite sufficient to prove that the hexane in petroleum is a normal paraffin, the constitution of which is expressed by the formula



Hexane from Mannite.

ERLENMEYER and WANKLYN obtained this hydrocarbon by heating the secondary hexyl iodide obtained from mannite with zinc and water. I found it more convenient to act on the iodide with zinc and hydrochloric acid in the cold. To prepare it, a flask is filled with finely granulated zinc, the iodide is added, and then so much dilute hydrochloric acid that the zinc is not completely covered. The vessel must be immersed in cold water, or else a very violent reaction sets in. After a few hours the heavy iodide has disappeared and a light layer swims on the top, which, when subjected to distillation, was found to consist of a liquid boiling at about 70° , besides a smaller quantity of a body boiling at above 190° .

The liquid boiling at 70° had the odour of hexene, and the reaction with bromine showed that this body was present. In order to remove it, bromine was added drop by drop to the well-cooled liquid as long as its colour disappeared, and then hexane and hexene dibromide separated by fractional distillation.

The hexane from mannite, after being purified by treatment with nitric and sulphuric acids and rectification over sodium, is a mobile liquid, having the faint but characteristic odour of the paraffins. It boils constantly at 71.5° , and has at 17° the specific gravity 0.6630.

By acting with chlorine on its vapour a product is obtained, the greater portion of which boils at 126° to 128.5° , and a smaller at 128.5° to 130° . Besides these, higher

chlorinated products had been formed, but only in a small quantity. From the liquid boiling between 126° and 130° , the alcohols were prepared and separated by fractional distillation into two portions; one, being about $\frac{2}{3}$ of the whole, boiled constantly at 140° to 141° ; between 141° and 150° only a small quantity distilled, the remainder coming over between 150° and 153° . The products of oxidation were the same as those from the petroleum hexane, viz. *methyl-butyl ketone* and *caproic acid*.

The methyl-butyl ketone boiled constantly at 127° , and appears to be identical with that which ERLÉNMEYER and WANKLYN obtained from the secondary hexyl alcohol; on further oxidation it yields *acetic acid* and *normal butyric acid*, the presence of the latter being proved by the characteristic properties of the calcium salt.

The analyses of the silver salts, which were obtained as described above, gave the following results:—

Calculated for silver butyrate	55.38 per cent.
1st fraction, 0.375 gave 0.1975 Ag=	55.35 per cent.
2nd „ 0.1241 „ 0.0685 Ag=	55.19 per cent.
3rd „ 0.1365 „ 0.079 Ag=	57.88 per cent.
4th „ 0.183 „ 0.118 Ag=	64.48 per cent.
Calculated for silver acetate	64.67 per cent.

The caproic acid, of which I obtained only a small quantity, had the same odour as that from petroleum, and the same boiling-point, viz. 201° to 204° .

0.1655 of silver caproate, which formed small needles, gave 0.0803 Ag=48.5 per cent., the calculated quantity being 48.43 per cent.

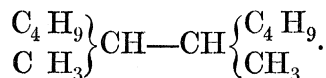
The calcium salt had the same properties as that from petroleum; the barium salt, however, was not amorphous, but crystallized most readily in plates or broad needles.

On decomposing the monochlorides with potassium acetate about equal quantities of the acetic ethers and hexene were formed, and by oxidizing the mixture of the two alcohols the quantity of acetone was double that of the caproic acid. Now, as the hexene was no doubt derived from the secondary chloride, it appears that by the action of chlorine upon the hydrocarbon $\frac{1}{6}$ is converted into the primary chloride, and $\frac{5}{6}$ into the secondary one.

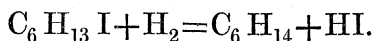
The hexane of mannite and some of the derivatives boil a few degrees higher than the corresponding compounds from petroleum, and also the barium salts of the two caproic acids exhibit a decided difference. The hexane from petroleum is certainly not a pure compound; but whether this is the cause of the difference between the two hydrocarbons, or whether we have here a case of fine isomerism, for which an explanation has to be found, it is at present impossible to decide; the formation of acetic and normal butyric acids, however, proves that the hexane from mannite is also a normal hydrocarbon.

The products formed by acting with zinc and hydrochloric acid on hexyl iodide consist

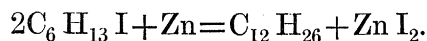
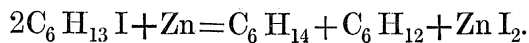
of hexane, besides smaller quantities of hexene and a higher boiling liquid. The latter compound is a *dihexyl*, $C_{12}H_{26}$; it boils at 201° , and has at 17° the specific gravity 0.7738. It has the same boiling-point as the dihexyl obtained by the electrolysis of ænanthyllic acid, which, as I shall show further on, is also a normal hydrocarbon. Whether these two hydrocarbons are identical or not has to be yet decided. The dihexyl from mannite might possibly have the following constitution:—



By acting with zinc and hydrochloric acid upon hexyl iodide the following is the principal reaction:—



But besides that also the following decompositions occur:—



Normal Dipropyl, C_6H_{14} .

To obtain this compound, allyl alcohol was first prepared from glycerine by TOLLEN'S method* and converted into propyl alcohol†, from which propyl iodide was obtained, boiling at 100° to 102° . On adding anhydrous ether and sodium to this iodide no reaction took place, either at the ordinary temperature or at the boiling-point of the mixture. To effect a complete decomposition, the substances had to be heated together in closed tubes to 140° – 150° .

Pure dipropyl boils at 69° to 71° , and has at 17° the specific gravity 0.6630. It has, therefore, the same physical properties as the hexane from mannite, and from its formation it follows that it has also the same constitution. The quantity obtained was not sufficient to examine its derivatives.

Normal Heptyl Hydride, or Heptane, C_7H_{16} .

This hydrocarbon was first discovered by me in the light oils from cannell coal-tar‡, and afterwards I found it in large quantities in the petroleum from Pennsylvania§. WARREN has since shown that, besides this body, petroleum also contains an isomeric heptane, which boils at $90^{\circ}.4$ ||; and my later researches have led me to the same conclusion¶. This lower-boiling heptane is always present, but in smaller quantities than the normal hydrocarbon. As the boiling-points of the two isomerides differ only by 10° , their complete separation is a very difficult and tedious process. By a very carefully

* Ann. Chem. Pharm. vol. clvi. p. 104.

† Chem. Soc. Journ. vol. xv. p. 419.

|| Chem. News, vol. xiii. p. 74, from Mem. Amer. Academy.

† Ibid. vol. clix. p. 92.

§ Chem. Soc. Journ. [2] vol. i. p. 216.

¶ Proc. Roy. Soc. vol. xiv. p. 468.

conducted fractional distillation I succeeded in obtaining about one litre of normal heptane, 600 cub. centims. of which distilled at $97^{\circ}5$ to 98° , and the remainder at 98° to 99° . According to PELOUZE and CAHOURS, the heptyl hydride from petroleum boils at 92° to 94° ; but this body was a mixture of the two isomerides.

The heptyl chlorides boil at 145° to 160° , the principal fraction distilling, as I have formerly stated, at about 150° . The acetates which boil between 175° and 185° yielded, by acting on them with caustic potash, the two alcohols. The secondary heptyl alcohol boils at 160° to 162° , and the primary one at 170° to 175° . The former yields on oxidation *methyl-pentyl ketone*, $\left. \begin{matrix} \text{C}_5\text{H}_{11} \\ \text{C}_5\text{H}_{11} \end{matrix} \right\} \text{CO}$, and the latter *œnanthylic acid*, $\text{C}_7\text{H}_{14}\text{O}$.

Methyl-pentyl ketone has a pleasant smell, like all these acetones; it boils at 150° to 152° , and combines with the bisulphites of the alkaline metals. By oxidizing it with chromic acid, acetic acid and pentylic acid are formed. The latter was isolated by repeated distillation of the aqueous solution of the two acids, the pentylic acid always coming over with the first portions, whilst the acetic acid is left in the residues, from which, by boiling them with silver carbonate, silver acetate was obtained, crystallizing in shining flat needles.

0.585 of silver acetate left on ignition 0.378 Ag = 64.62 per cent.

The distillate containing the pentylic acid was neutralized with sodium carbonate, the solution evaporated, and the residue decomposed by sulphuric acid. The acid, after being dried with phosphorus pentoxide and freed by distillation from a little acetic acid, boiled at 183° to 187° , and smelt exactly like that obtained from pentane. The calcium salt separates as a crystalline precipitate on heating the cold saturated solution to about 70° , as well as on cooling down the boiling saturated solution to that temperature. The barium salt crystallized from the hot saturated solution in shining plates.

0.338 of this salt lost, at 180° , 0.0230 H_2O .

Calculated for $(\text{C}_5\text{H}_9\text{O}_2)_2\text{Ba} + \frac{1}{2}\text{H}_2$.
7.4 per cent.

Found.
6.8 per cent.

The dry residue left on ignition 0.1835 Ba CO_3 .

Calculated.
40.4 per cent. Ba

Found.
40.2 per cent.

The œnanthylic acid was found to be identical with that obtained from castor-oil. That from heptane boiled at 219° to 222° , and the acid prepared from castor-oil at 219° to 221° . On treating equal quantities of the two acids with water and barium carbonate, and evaporating the two solutions to exactly the same volume, thin iridescent plates appeared on cooling, which grew into large plates and broad needles; both salts are anhydrous.

(1) 0.467 of the salt from heptane lost, at 180° , 0.003 H_2O ; the residue left on ignition 0.232 Ba CO_3 .

(2) 0.615 of the salt from castor-oil lost, at 180° , 0.003 H_2O , and the residue gave 0.306 Ba CO_3 .

Calculated for $(\text{C}_7\text{H}_{13}\text{O}_2)_2\text{Ba}$. 34.43 per cent. Ba	Found.	
	I.	II.
	34.5 per cent.	34.6 per cent.

The mother-liquor of the barium salt from heptane gave with silver nitrate a white precipitate, which crystallized from boiling water in indistinct needles.

0.387 of this salt gave 0.178 $\text{Ag}=46.0$ per cent.

Calculated for $\text{C}_7\text{H}_{13}\text{O}_2\text{Ag}=45.6$ per cent.

As the secondary heptyl alcohol yields on oxidation *acetic acid* and *pentylic* or *normal valerianic acid*, it follows that the heptane is a normal hydrocarbon, having the constitution



α -Nanthylic acid is consequently a normal acid, and dihexyl, which BRAZIER and GOSLETH obtained by the electrolysis of potassium α -nanthylate, is therefore a normal hydrocarbon, to which I give the name *dodecane*, $\text{C}_{12}\text{H}_{26}$.

Normal Dibutyl or Octane, C_8H_{18} .

Normal butyl iodide, prepared by LIEBEN's method from butyric acid, and boiling at 128° to 130° , is easily acted upon by sodium in the cold. After a sufficient quantity had been gradually added, the mixture was heated for some hours, and then the hydrocarbon distilled off and purified by the well-known methods.

Dibutyl boils at 123° to 125° , and has at 17° the specific gravity 0.7032. These are exactly the properties of the octane which I have obtained from methyl-hexyl carbinol* and from sebacic acid†, and of that which ZINCKE prepared from his primary octyl alcohol‡. As the properties of these hydrocarbons of different origin agree so very closely, it appears almost certain that they are identical. If so, the dioctyl, $\text{C}_{16}\text{H}_{34}$, which ZINCKE obtained as a by-product in preparing octane is also a normal paraffin, which I call *hecdecane*.

We are now acquainted with the following normal paraffins or homologues of marsh-gas, in which the carbon atoms are linked together in a single chain§.

* Proc. Roy. Soc. vol. xvi. p. 376.

† Ibid.

‡ Ann. Chem. Pharm. vol. clii. p. 1.

§ Comp. Proc. Roy. Soc. vol. xix. p. 488.

		Boiling-points.		Difference.
		Mean found.	Calculated.	
C H ₄	Methane			
C ₂ H ₆	Ethane			
C ₃ H ₈	Propane			
C ₄ H ₁₀	Butane	1°	1°	37
C ₅ H ₁₂	Pentane	38	38	33=37-4
C ₆ H ₁₄	Hexane	70	71	29=33-4
C ₇ H ₁₆	Heptane	99	100	25=29-4
C ₈ H ₁₈	Octane	124	125	4×19
C ₁₂ H ₂₆	Dodecane	202	201	14×19
C ₁₆ H ₃₄	Hecdecane	278	278	

In calculating the boiling-points, it was assumed, as appears to be the case, that the difference decreases regularly by 4 until it reaches the well-known difference 19°.