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XLVIII.—*Methyl-hexyl Carbinol.*

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SEVERAL years ago I showed that the so-called capryl alcohol, which is produced by distilling castor-oil soap with soda, is methyl-hexyl carbinol. Afterwards I found that the octane obtained from it has the same specific gravity and the same boiling-point as the dibutyl which I prepared from normal butyl iodide. From this I concluded that these two paraffins were most probably identical. If this be correct, the alcohol must on oxidation yield normal caproic acid.

A decision of these questions is now very simple, since Lieben and Rossi have published their beautiful researches on the caproic acids of different origin.

The alcohol which I used for my new research was obtained from Trommsdorff in Erfurt. It was almost pure, and contained, besides some methyl-hexyl ketone, only a very small quantity of high-boiling bodies. I purified it first by fractional distillation, and found that by far the greater portion boiled constantly at 176° — 177° under a pressure of 734·2 mm., and the whole column of mercury being immersed in the vapour.

I found, however, that this portion, as well the higher-boiling fractions, contained one or more ketones, and as the presence of these might affect the results of my research, I treated the alcohol repeatedly with a concentrated solution of acid sodium sulphite. Thus purified, the alcohol boiled at 177° — 178° under a pressure of 755 mm. The ketone which I isolated from the sodium sulphite compound contained either none or only a mere trace of other ketones: for that obtained from the highest boiling fraction boiled at 173° — 175° , while pure methyl-hexyl ketone boils at 173° . All these and the following determinations were made with the whole column of the thermometer surrounded by the vapour.

The caproic acid obtained from the pure alcohol boiled, under a pressure of 755 mm., at 204° — 206° . It was converted into the calcium and barium-salts, which were analysed and their solubility determined.

Calcium caproate, $\text{Ca}(\text{C}_6\text{H}_{11}\text{O}_2)_2 + \text{H}_2\text{O}$, is a little more soluble in hot than in cold water, and is obtained by the spontaneous evaporation of its solution in small thin glistening plates or broad needles. 100 *parts by volume* of its solution saturated at 15° contain 2·700 parts by weight of the anhydrous salt, which was determined in the form of oxide.

Normal calcium caproate has exactly the same properties. Lieben and Rossi found that 100 *parts by weight* of its solution saturated at 18.5° contain 2.707 parts of the anhydrous salt.

Barium caproate $\text{Ba}(\text{C}_6\text{H}_{11}\text{O}_2)_2$ is anhydrous, and much more soluble in hot than in cold water. From a hot saturated solution it crystallises in feathery tufts. These are the properties of the salt of the normal acid. 100 *parts by volume* of its solution saturated at 15° , contain 8.122 parts by weight of the salt, which was determined as barium carbonate. According to Lieben and Rossi, 100 *parts by weight* of a solution of their salt, saturated at 18.5° , contain 8.4967 parts.

From these results it follows that the caproic acid from methyl-hexyl carbinol is the normal compound, and consequently that the octane prepared from this alcohol is a normal paraffin.

Now, I have shown that, by the action of chlorine on normal paraffins, a primary chloride, and a secondary chloride, containing the group $-\text{CHCl}-\text{CH}_3$ are produced simultaneously: for on converting them into the alcohols, and oxidising these, a large quantity of acetic acid is obtained, besides the other acids which theory indicates. But on treating the octane from methyl-hexyl carbinol in the same way, I obtained, besides a small quantity of an octylic acid, a mixture of lower fatty acids (probably propionic and valerianic acids), but not a trace of acetic acid could be detected.

The question, therefore, arises, why does this octane differ from the other normal paraffins? My next endeavour will be to elucidate this point.

I formerly stated that methyl-hexyl carbinol boiled at 181° . I believe, however, that my last observation is more correct: for I had this time much more material at my disposal than formerly, and besides, it appears to be a law that a normal secondary alcohol containing the group $-\text{CH}(\text{OH})-\text{CH}_3$ boils at the same temperature as that normal primary alcohol which contains one atom of carbon less. A glance at the following table will show this, only such alcohols having been selected as have been more minutely studied:—

	Boiling point.		Boiling point.
$\text{C}_3\text{H}_7.\text{OH} \dots\dots$	$97^{\circ}-98^{\circ}$	$\text{C}_3\text{H}_6(\text{OH})\text{CH}_3 \dots\dots$	$96^{\circ}-98^{\circ}$
$\text{C}_6\text{H}_{11}.\text{OH} \dots\dots$	137°	$\text{C}_6\text{H}_{10}(\text{OH})\text{CH}_3 \dots\dots$	136°
$\text{C}_7\text{H}_{15}.\text{OH} \dots\dots$	$115.5^{\circ}-177.5^{\circ}$	$\text{C}_7\text{H}_{14}(\text{OH})\text{CH}_3 \dots\dots$	$177^{\circ}-178^{\circ}$

This tends to show that any elevation of the boiling-point which ought to be produced by substituting methyl for hydrogen, is completely equalized by the diminution, which, as Naumann has shown, is caused by the shifting of the oxygen towards the middle of the chain of atoms. As a further proof of this, we find that both primary isobutyl alcohol and methyl-isobutyl carbinol boil at 108° .