XII. *On the Normal Paraffins.*—Part III.

By C. SCHORLEMMER, *F.R.S., Professor of Organic Chemistry in Owens College, Manchester.*

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THE isomeric monochlorides obtained from the normal paraffins existing in petroleum yield by the abstraction of hydrochloric acid a mixture of olefines, one portion of which readily combines with hydrochloric acid in the cold, whilst the other is not changed, even if it be left in contact with the acid for weeks, and only unites with it on heating.*

The chlorides which are formed in the cold boil with partial decomposition and at a lower temperature than the others, which distil without undergoing any change, and, as MORGAN has shown, have the general formula, $CH_3-CHCl-C_nH_{2n+1}$.† They are, therefore, derivatives of the olefines having the constitution $CH_2=CH-C_nH_{2n+1}$ or $CH_2=CHR$, and which, as LE BEL‡ has also shown, combine with hydrochloric acid only on heating.

The constitution of the olefines from petroleum which unite with the acid in the cold is not yet known. I have formerly pointed out that possibly they are not derived from normal paraffins, and this view seems to find confirmation in the observation of LE BEL that the property of combining with cold hydrochloric acid belongs to the hydrocarbons which have the general formulæ $CH_2=CRR'$ and $CHR=CRR'$.

On the other hand, I showed that the formation of isomeric olefines might be explained without making the assumption that the normal paraffins from petroleum contained an admixture of isomerides, but that in order to decide this question an absolutely pure paraffin must be used.§

For reasons which are not far to seek, I selected for this investigation the normal hexane from mannite, which possibly might, by the action of chlorine, yield the following monochlorides :—

(1) $CH_3-CH_2-CH_2-CH_2-CH_2-CH_2Cl$.
(2) $CH_3-CH_2-CH_2-CH_2-CHCl-CH_3$.
(3) $CH_3-CH_2-CH_2-CHCl-CH_2-CH_3$.

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* Journ. Chem. Soc., 1873, p. 323.

† *Ibid.*, 1875, p. 301.

‡ Bull. Soc. Chim. (2), vol. xxviii., p. 460.

§ Journ. Chem. Soc., 1875, p. 306.

I have already shown that the first two of these compounds are thus formed. The following method seemed to me capable of determining whether the third is also produced.

On heating the chlorides with an alcoholic solution of potash they are converted into olefines, and thus the three following hexylenes might be formed :—

Butylethylene.	$CH_3-CH_2-CH_2-CH_2-CH=CH_2$
Methylpropylethylene	$CH_3-CH_2-CH_2-CH=CH-CH_3$
Diethylethylene	$CH_3-CH_2-CH=CH-CH_2-CH_3$

The first of these does not combine with hydrochloric acid in the cold, as MORGAN has found, nor does the hexylene which is obtained by decomposing the secondary hexyl iodide from mannite, as LE BEL and WASSERMANN have shown. This hydrocarbon, however, is not butylethylene, as they assumed, but consists of methylpropylethylene.*

If, therefore, normal hexane from mannite yields a hexylene combining with hydrochloric acid in the cold, it could be only diethylethylene, which might further be identified by conversion into the corresponding secondary alcohol. This ought to consist of ethylpropyl carbinol, and should yield on oxidation only propionic acid.

This is the programme which I intended to follow in my research ; the results obtained were, however, quite unexpected.

In order to prepare pure hexane, I distilled mannite with an excess of fuming hydriodic acid and the addition of amorphous phosphorus. A good yield of secondary hexyl iodide is thus easily obtained. The iodide was reduced by the method already described, and the hexane separated from some hexylene and dodecane, which are formed at the same time.†

By the action of chlorine on the pure hydrocarbon a mixture of monochlorides, boiling between 121° and 134°, was obtained, which was heated with an alcoholic solution of potash to 100°. The reaction went on rather quickly, and was soon completed. The product consisted principally of hexylene, but contained also a mixture of ethylhexyl ethers.

The hexylene was left in contact with an excess of fuming hydrochloric acid for several weeks, the mixture being contained in a well-closed bottle and kept in the dark. The excess of acid being removed, the product was, after washing and drying, distilled. Of course I expected to find a considerable quantity of uncombined hexylene to be present ; but, to my great surprise, *the whole product boiled constantly and without the least decomposition* at 124—125°, while the chloride which MORGAN obtained by the action of cold hydrochloric acid on the hexylenes from petroleum distilled at 116—118° with the evolution of hydrochloric acid.

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* O. HECHT, Deut. Chem. Ges. Ber., Bd. xi., p. 1152.

† Phil. Trans., Vol. 162, p. 111.

In order to elucidate the constitution of the chloride, it was heated with anhydrous lead acetate and glacial acetic acid to 125°. A complete decomposition was thus easily effected, and, besides hexyl acetate, a crystalline compound was formed, consisting of lead acetochloride Pb $(C_2H_3O_2)$ Cl, a salt which has been discovered by CARIUS.

The hexyl acetate was thrown out of solution by the addition of water, and without further purification converted into the alcohol by heating it with a concentrated solution of potash. The product was found to contain a little hexylene, which was easily got rid of; the alcohol, after being dried over ignited potassium carbonate, distilled between 130° and 140°. By repeated fractional distillation and drying over potassium carbonate, it was separated into a portion boiling at 130—135°, which was a little larger than the other, boiling between 135° and 140°; but no body having a constant boiling point could be isolated, although the chloride boiled within one degree. Perhaps it was after all a mixture, and, if so, the alcoholic liquid would be a mixture of methylbutyl carbinol and ethylpropyl carbinol.

In order to decide this question each portion was subjected to fractional oxidation, as I expected that, in case two ketones were formed, one might be more readily oxidised than the other. I employed, therefore, in each operation only so much of the chromic acid solution that but a small quantity of fatty acids could be formed, and separated these in the same way as described in my former papers.

The results were, however, the same as those formerly obtained: the formation of acetic acid and butyric acid could be easily proved both qualitatively and quantitatively, but no propionic acid could be found; and if any was present, its quantity must have been exceedingly small.

I have already stated that in the preparation of hexylene a small quantity of ethylhexyl ethers is formed. As they could not be separated by fractional distillation, I heated them with hydriodic acid, and thus obtained, besides ethyl iodide, a liquid boiling between 168° and 178°—*i.e.*, the boiling points of the common secondary and the normal primary hexyl iodide.

The results of this research confirm thus far those which I had already obtained seven years ago—viz.: that by the action of chlorine on the normal hexane from mannite, normal hexyl chloride is formed, together with a larger quantity of the secondary chloride $C_4H_9.CHCl.CH_3$. But it is certainly very remarkable that the hexylene obtained from them, or perhaps only from the secondary compound, combines so readily with hydrochloric acid in the cold, while the hexylene obtained by perfectly analogous reactions from normal petroleum hexane unites with the acid only by heating under pressure; and yet the two chlorides thus obtained have apparently the same constitution.

I have already, in my first paper, pointed out some other differences existing between the two hexanes, and said:—

"The hexane from 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."[*]

I believe the results of my present research speak strongly in favour of the latter view. Further experiments are, however, required to elucidate these points, as well as the constitution of the olefines from petroleum which combine readily with hydrochloric acid in the cold.

Another point which wants clearing up is the fact that the normal paraffins from petroleum have a higher specific gravity than those obtained from any other source. This is probably due to some admixture, for I found that on treating hexane with hot nitric acid[†] the specific gravity of the non-oxidised portion decreased and became at last constant, being 0·663 at 17°, or the same as that of hexane from mannite and of normal dipropyl.[‡] The normal paraffins from petroleum appear, therefore, not to be pure compounds; and for several reasons I am inclined to belive that petroleum, after being freed from olefines, aromatic hydrocarbons, and those of other series, consists of an inextricable mixture of isomeric and homologous paraffins, in which, however, the normal hydrocarbons preponderate. This would certainly explain why it is so extremely difficult to isolate from it bodies having a constant boiling point,[§] but not why the normal hexylene obtained from petroleum will not unite with hydrochloric acid under the same conditions as that prepared from mannite.

A continuation of these researches has been already commenced. My friend THORPE, who made the most interesting discovery that the terebinthinate exudation of *Pinus Sabiniana* contains a large quantity of normal heptane,[||] has kindly invited me to join him in the chemical investigation of this hydrocarbon. At the same time we shall compare it with other "normal" heptanes from different sources.

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[*] Phil. Trans., Vol. 162, p. 119.

[†] Proc. Roy. Soc., vol. xvi., p. 372.

[‡] Phil. Trans., Vol. 162, p. 120.

[§] Journ. Chem. Soc., 1875, p. 306.

[||] Journ. Chem. Soc., 1879, p. 296.