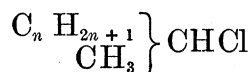IV. *On the Normal Paraffins.*—Part II.
By C. Schorlemmer, *F.R.S., Professor of Organic Chemistry in the Owens College, Manchester.*

In my first paper on this subject I have shown that by the action of chlorine on a normal paraffin a primary chloride and a secondary one of the general formula

$$\left.\begin{array}{c} C_n\,H_{2n+1} \\ CH_3 \end{array}\right\} CHCl$$

are formed simultaneously.*

I subsequently pointed out that other secondary chlorides, which are indicated by theory, are also probably produced at the same time.† I am still engaged with an investigation of this subject. It appeared of interest also to examine the action of bromine on the paraffins. The present paper contains the first results of this research.

Cahours and Pelouze state in their well-known paper on Caproyl Hydride (Hexane) that, while chlorine converts it into caproyl (hexyl) chloride $C_6\,H_{13}\,Cl$, bromine at once replaces two atoms of hydrogen, the dibromide $C_6\,H_{12}\,Br_2$ being formed; if, therefore, an equal number of molecules of the two bodies act on each other, one half of the hydrocarbon is not attacked.‡

Soon after I examined the action of bromine on heptane, and found that when a mixture of the two substances is exposed to the sunlight, or heated in sealed tubes to 100°, hydrobromic acid is slowly evolved, but the substitution products thus formed began to decompose at 110°, hydrobromic acid being given off and carbonaceous matter left behind.§

The satisfactory results which I obtained by acting with chlorine on the vapour of the boiling hydrocarbons, which were thus almost entirely converted into monochlorides, induced me to try the action of bromine under similar conditions.

The apparatus which I employed was very similar to that described in my former paper. It consisted of a flask holding about one litre, which was closed with a doubly-perforated cork, provided with a bulb-funnel, with glass stop-cock, the tube of which reached half-way down the neck of the flask, which was connected with the lower end of

* Phil. Trans., Vol. 162, p. 111.
† Journ. Chem. Soc., N. S., vol. xiii. p. 306.
‡ Compt. Rend., tom. liv. p. 1241.
§ Journ. Chem. Soc., vol. xvi. p. 216.

a reversed LIEBIG's condenser. As the hydrobromic acid which is evolved during the reaction carries off some of the volatile hydrocarbons, the upper end of the condenser was bent downwards and connected with a flask containing a solution of caustic potash, in which, however, the tube did not dip, as if that had been the case, the liquid would have been sucked back into the hydrocarbon when the reaction slackened ; one absorption flask was found sufficient to condense the hydrobromic acid completely. To ascertain, in the beginning of each experiment, whether all parts of the apparatus were tight, the cork of the flasks containing the soda solution was provided with a bent tube dipping into a little water.

I. *Normal Hexane.*

About 300 cub. centims. were heated in the large flask, and when briskly boiling, the stop-cock of the funnel-tube containing the bromine was so far turned that the liquid running down the tube was completely converted into vapour. On a bright day the colour of the bromine disappeared at once ; on a dull day, however, the action was much slower and ceased altogether in gas-light. It was very curious to observe how, on a clear day, when the sun was suddenly obscured by dark clouds, the flask became filled with brown vapours, which disappeared again as quickly as the clouds before the sun.

The action was stopped before one-half of the hydrocarbon was attacked, and the product shaken with solid caustic potash, to free it from hydrobromic acid. On distilling, the excess of hexane came over first ; the thermometer then began to rise, but even below 100° decomposition commenced, hydrobromic acid being evolved and a brominated liquid distilling over, while a black mass was left behind. In order to prevent this decomposition another portion was distilled with steam, but with no better success ; a tarry or carbonaceous matter was left behind, and the distillate contained besides hexane, brominated hexane, hexene, and hydrobromic acid.

On submitting the brominated product to fractional distillation some of it began to decompose again, with the evolution of hydrobromic acid and blackening. But on continuing the distillations this decomposition gradually ceased, and a large quantity of a colourless liquid, boiling at 143—145°, and having a pungent and aromatic smell, could be isolated without difficulty. The low boiling point shows that this body was not primary hexyl bromide, which boils at 155·5°.* Besides it, a small quantity of a higher boiling liquid was obtained, which, however, by further distillations yielded some more of the bromide boiling at 143—145°, while the highest boiling portion completely decomposed. The fractions distilling between 68° (the boiling point of hexane) and 143° were very small, and consisted of mixtures of the hydrocarbon and the bromide, of which some more could be isolated by carrying on the distillation.

The hexyl bromide was decomposed by heating it in sealed tubes with potassium

* Lieben and Janecek, Liebig's Ann., 187, p. 126.

acetate and glacial acetic acid ; the reaction commenced at 100°, proceeded rapidly at 120°, but to ensure a complete decomposition it was found necessary to heat to 150°.

The product consisted of a hexyl acetate and a little hexene, which were readily separated by distillation. The acetate possesses the characteristic smell of the acetic ethers, and boils at 146—150°; it was converted into the alcohol by heating it with caustic potash and a little water ; the hexyl alcohol thus formed boiled, after drying it over potassium carbonate and removing a little hexene by distillation, at 136—140°, and smelled like methylbutyl carbinol. It was oxidised in the cold by chromic acid solution in the manner described in my last paper. A neutral liquid was thus obtained possessing the odour of methylbutyl ketone ; it began to boil at 127°, and the greater portion distilled between this temperature and 130° ; the thermometer then rose rapidly, and the residue had the odour of a compound ether, and consisted, as the following experiments show, undoubtedly, of hexyl butyrate. Besides these compounds a very small quantity of acids had also been formed which, judging by the smell, consisted of acetic acid and butyric acid ; a few drops of dilute soda were sufficient to neutralise them.

The ketone and ether were again mixed and heated with the oxidising mixture, which contained twice as much water as in my previous experiments, nearly to the boiling point, and the acids converted in the sodium salts, as described in my former paper. Two series of experiments were made to ascertain their composition.

As it appeared very probable that only acetic acid and butyric acid were formed, the sodium salts were distilled with sulphuric acid and a little water, and the distillate after diluting with much water repeatedly distilled, the first distillates and the residues being kept separately. The first distillate and the last residue were then converted into the silver-salts by boiling them with silver carbonate, and the silver determined by ignition.

0·3241 of salt from the first distillate, crystallising in small needles, gave 0·1793 silver.

Calculated for silver butyrate.	Found.
55·38 per cent. Ag	55·32

0·2647 of salt from the last residue, forming larger glistening needles, gave 0·1690 silver.

Calculated for silver acetate.	Found.
64·67 per cent. Ag	63·84

The intermediate distillates were again mixed and neutralised with sodium carbonate. The acids were liberated from this mixture in four fractions by the method formerly described :—

				Salt.	Silver.	Per cent. Ag.
(1) Fraction—Indistinct needles ..			..	0·1892	0·1045	55·23
(2) ,, Small needles		..	..	0·1091	0·0612	56·09
(3) ,,	,,	,,	..	0·2176	0·1290	59·29
(4) ,,	,,	,,	..	0·1842	0·1182	64·17

A portion of the first distillate was also converted into the calcium-salt, which gave the characteristic reactions of normal calcium butyrate.

From these experiments it follows that by the action of bromine on normal hexane, the secondary hexyl bromide,

$$\left.\begin{array}{c} C_4H_9 \\ CH_3 \end{array}\right\} CH\,Br$$
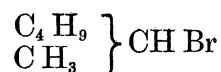
or *methyl-butyl-carbyl bromide* is formed.

II. *Normal Heptane.*

This hydrocarbon is more readily attacked by bromine than hexane, and the reaction goes on, but of course very slowly, in artificial light. This is probably due to the higher temperature at which the substitution takes place. The phenomena are however in both cases quite similar. A portion of the product is decomposed by distillation, carbonaceous matter, hydrobromic acid, and heptene being formed, and a heptyl bromide distilling between 165—167° is obtained, having a pungent and aromatic odour.

It was analysed with the following result :—

0·326 gave 0·3414 silver bromide.

Calculated.	Found.
44·67 per cent. Br.	44·57

On converting it into the acetate a little heptene was formed; the pure acetate boils at 169—171°, and has a pleasant fruity odour. By heating it with caustic potash a little heptene was again obtained, and secondary heptyl alcohol or *methyl-pentyl carbinol,*

$$\left.\begin{array}{c} C_5H_{11} \\ CH_3 \end{array}\right\} CH\cdot OH.$$
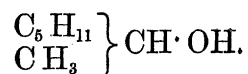
This alcohol boils at 155—157°, and yields on oxidation in the cold methylpentyl ketone boiling at 150—152°, and a higher boiling compound ether. The products are converted by further oxidation into normal pentylic acid and acetic acid, as the following analyses of the silver salts show :—

						Calculated for silver pentylate 51·67.		
						Salt.	Silver.	Per cent. Ag.
(1)	Fraction—Small woolly needles				..	0·0741	0·0351	49·16
(2)	,,	,,	,,	,,	..	0·1261	0·0649	51·48
(3)	,,	,,	,,	,,	..	0·1795	0·0943	52·53
(4)	,,	,,	,,	,,	..	0·2591	0·1448	55·89
(5)	,,	,,	,,	,,	..	0·2623	0·1668	63·59
(6)	,,	Glistening needles			..	0·2716	0·1741	64·10

Calculated for silver acetate ..   64·67

The analysis of the first fraction differs from the calculated percentage 1·5 per cent. This is easily explained.   I have already shown that the petroleum from which the heptane was obtained contains also an isoctane $C_8 H_{18}$ boiling only 15° higher than normal heptane.   The latter undoubtedly contains some of the former, and its presence gives rise to the formation of a fatty acid containing more carbon than pentylic acid.

That the latter acid is the normal compound was proved by converting it into calcium pentylate; a cold saturated solution of this salt deposits on heating small glistening plates, which, after cooling, gradually dissolve again.

As result of this investigation it appears that by the action of bromine on normal paraffins only secondary bromides of the general formula,

$$\left. \begin{array}{c} C_n H_{2n+1} \\ CH_3 \end{array} \right\} CH\, Br$$
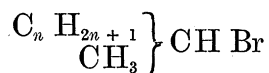
are produced, but not a trace of primary bromide, or that the methyl groups which are present in these hydrocarbons, and which are readily attacked by chlorine, are not touched by bromine at all.

In addition to the secondary bromides other products are formed, which on distillation either decompose completely, or are resolved into hydrobromic acid and non-saturated hydrocarbons, which are probably olefines.   The formation of these may be explained by assuming that besides the secondary bromides which I have described, others, which the theory indicates, are also formed, and that the latter, by the action of heat, split up into an olefine and hydrobromic acid.   I have endeavoured to isolate these olefines, which I obtained mixed with paraffins, by adding bromine very carefully to the well-cooled mixture as long as its colour disappeared.   The liquid, after being shaken with solid potash to remove free bromine and a little hydrobromic acid, was distilled by itself and with steam, but in both cases the bromides underwent complete decomposition, with the formation of a black mass and hydrobromic acid.

I hope, however, by continuing this research, to ascertain the nature of the products which are formed together with the volatile bromides.