XXV.—*On the Derivatives of Hydride of Heptyl.*

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SOME years ago, Berthelot showed that, by the action of chlorine, on marsh gas, chloride of methyl is formed, from which, by double decompositions, other methyl-compounds can be obtained.* This method is a general one, and is applicable to all the hydrocarbons which are homologous with marsh gas, and I have already stated in a former communication,† that in this way I obtained *acetate of heptyl* and *heptylic alcohol*, from the corresponding hydride which I had previously found in the light oils from cannel-tar, and in larger quantities in rectified American petroleum. The constitution of this petroleum is, as I have shown in a communication read before the Literary and Philosophical Society of Manchester,‡ analogous to that of the oils from cannel-coal, inasmuch as it consists chiefly of the hydrides of the alcohol-radicles, but also contains benzol and homologous hydrocarbons.

The hydride of heptyl from petroleum, possesses in every respect

* Compt. rend., xlv, 916.

† Chem. Soc. J., xv, 419.

‡ Proceed. Lit. Phil. Soc., Manchester, March 13, 1863.

identical properties with that from cannel tar; it boils at 98°C ., the specific gravity is 0.7122 at 16°C .

Analysis: 0.1935 substance gave 0.5955 CO_2 , and 0.2810 H_2O .

Calculated.		Found.
C_7	84	83.93
H_{16}	16	16.13
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100		100.06
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Determination of vapour-density—

Balloon with air.	40.7955
Temperature of air	11°C .
Balloon with vapour	41.0960
Temperature of sealing. . . .	173°C .
Capacity of balloon	189.0 cbc.

These numbers give the vapour-density = 3.59; the theoretical density of hydride of heptyl = 3.46.

The hydride was converted into the chloride according to the beautiful method of Hugo Müller,* care being taken to avoid an excess of chlorine; the unattacked hydride was then distilled off, and the chloride of heptyl, $\text{C}_7\text{H}_{15}\text{Cl}$, was obtained from the portion boiling between 140 — 160° , by fractional distillation, as a colourless liquid boiling at 150°C .

When bromine is added to hydride of heptyl, and the mixture is exposed to direct sunlight, or heated in sealed tubes in the water-bath, hydrobromic acid is slowly evolved; but the action is much less energetic than in the case of chlorine; it may, however, be quickened by adding a little iodine. As soon as the colour of bromine had disappeared, the liquid was subjected to distillation; a large quantity of hydride passed over first; the temperature then rose slowly; and as soon as it reached 110°C ., the residue in the retort began to decompose, hydrobromic acid being given off, and a black charry matter left in the retort.

In order to convert the chloride of heptyl into the acetate, I heated it in sealed tubes with acetate of potassium and alcohol to 120° — 130°C . The greater part of the chloride is decomposed in a few hours, but in order to remove the last traces of chlorine

* Chem. Soc. Journ., xv, 41.

from the liquid, the mixture has to be heated to 200° C. for several days; in this part of the operation the tubes were nearly always found to explode.

I afterwards replaced the alcohol by glacial acetic acid, and found, that by heating the tubes in the air bath to 150° — 160° C. for twelve hours, all the chloride of heptyl was decomposed. The products are in both cases the same, namely, chloride of potassium, acetate of heptyl, and heptylene. The contents of the tubes were diluted with water; the light oily liquid which separated, was dried over chloride of calcium; and the heptylene, which boils at 95° C., easily separated by fractional distillation from the acetate of heptyl, boiling at 179° — 181° C. The latter is a colourless liquid of a pleasant smell, resembling that of pears. Analysis gave the following results:—

- I. 0.2185 grm. substance gave 0.5470 CO_2 and 0.2245 H_2O .
 II. 0.2445 grm. substance gave 0.6105 CO_2 and 0.2570 H_2O .

Calculated.			Found.	
			I.	II.
C_9	108	68.35	68.28	68.09
H_{18}	18	11.39	11.41	11.67
O_2	32	20.26	—	—
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	158	100.00		
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Distilled with a concentrated solution of potash, the acetate is decomposed, heptylic alcohol being formed. Heptylic alcohol $\text{C}_7\text{H}_{16}\text{O}$ is a colourless oily liquid, lighter than water, boiling at 164° — 165° C., and possessing a peculiar smell, which reminds one both of octylic and amylic alcohols.

The analysis of heptylic alcohol gave the following results:—

- I.—0.2035 substance taken
 0.5390 CO_2 obtained
 0.2625 H_2O ,,
 II.—0.2445 substance taken
 0.6480 CO_2 obtained
 0.3115 H_2O ,,

Calculated.			Found.	
			I.	II.
C ₇	84	72.40	72.23	72.28
H ₁₆	16	13.80	14.33	14.15
O	16	13.80	—	—
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	116	100.00		
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The acetate of heptyl and heptylic alcohol, which Bouis and Carlet obtained by the action of zinc and acetic acid on *cænanthol*,* possess the same boiling points as those I prepared from hydride of heptyl. It is noteworthy that the boiling-point of the acetate is about 10° higher, and that of the alcohol 10° lower, than the boiling-points calculated according to Kopp's law.

The action of iodine and phosphorus on heptylic alcohol yields the iodide of heptyl, a colourless liquid, heavier than water, which soon becomes brown in contact with the air, and boils at about 190° C. An alcoholic solution of nitrate of silver immediately decomposes it, and all the iodide separates out as iodide of silver, as the first of the following analyses shows.

I. 0.1695 iodide of heptyl was dissolved in alcohol, and an alcoholic solution of nitrate of silver added. It yielded 0.1490 AgI and 0.0125 Ag.

II. 0.3340 substance gave 0.4555 Co₂ and 0.2025 H₂O.

Calculated.			Found.	
			I.	II.
C ₇	84	37.17	—	37.19
H ₁₅	15	6.64	—	6.73
I	127	56.19	56.18	—
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	226	100.00		
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A concentrated aqueous solution of potash scarcely acts upon chloride of heptyl, even if they are heated together in sealed tubes to 180° C. for several days. Only a small quantity of heptylene is produced, and not the least trace of heptylic alcohol is formed.

Heptylene C₇H₁₄ is a colourless mobile liquid lighter than water, of rather a strong somewhat garlic-like smell, and boiling at 95° C.

0.2060 substance gave 0.6470 CO₂ and 0.2585 H₂O.

* Compt. rend., lv, 140.

	Calculated.		Found.
C ₇	84	85.71	85.66
H ₁₄	14	14.29	14.00
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	98	100.00	99.66
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With bromine it forms bibromide of heptylene C₇H₁₄Br₂, a liquid heavier than water, which decomposes on distillation, with evolution of hydrobromic acid and blackening, but volatilizes in presence of aqueous vapour, and condenses as a nearly colourless liquid, smelling like bibromide of ethylene, and having the above composition, as the following determinations of the amount of bromine show :—

I. 0.2590 substance gave 0.3665 AgBr and 0.0072 Ag.

II. 0.3555 substance gave 0.5020 AgBr and 0.0105 Ag.

	Calculated.		Found.	
			I.	II.
C ₇	84	32.56	—	—
H ₁₄	14	5.43	—	—
Br ₂	160	62.01	62.26	62.23
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	258	100.00		
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Heptylene also combines with hydriodic acid, on heating them together in sealed tubes to 100° C. for twelve hours. The hydriodate of heptylene C₇H₁₄HI closely resembles iodide of heptyl, but boils at about 170° C. or 20° lower; it readily turns brown in the air.

0.3290 gram. of hydriodate of heptylene was precipitated by an alcoholic solution of nitrate of silver, and gave 0.3230 AgI and 0.0075 Ag, corresponding to 55.73 % of iodine, instead of the calculated 56.19 %.

A larger quantity was treated in the same way, and the filtered liquid diluted with water. A small quantity of a liquid, lighter than water, and of a pleasant smell was obtained, which certainly consisted of, or at least, contained a large proportion of nitrate of heptylene C₇H₁₄.NO₃H, as by adding an alcoholic solution of potash, and gently heating, an abundant precipitate of nitrate of potassium was formed.

A concentrated solution of ammonia in alcohol decomposes the

chloride but slowly, even if heated in sealed tubes to 120° C. for several days. The chlorides of the different heptyl-ammoniums are formed, but chiefly chloride of heptylammonium, a salt readily soluble in water and alcohol, and crystallising from solution in small scales. On distilling it with a solution of caustic potash, heptylamine $C_7H_{17}N$ is obtained as a light oily liquid, with an ammoniacal, aromatic smell, possessing a burning taste, and boiling at 145° – 147° C. It is tolerably soluble in water, and separates out again on addition of caustic potash.

Analysis I.—0.2160 substance gave 0.1880 metallic platinum, corresponding to 0.0266 of nitrogen.

II.—0.1450 substance gave 0.3870 CO_2 and 0.2000 H_2O .

Calculated.			Found.	
			I.	II.
C ₇	84	73.04	—	72.79
H ₁₇	17	14.79	—	15.32
N	14	12.17	12.31	—
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	115	100.00		
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The platinum-salt is slightly soluble in cold water, freely soluble in hot water, and dissolves readily in alcohol and ether, crystallising from those solutions in small yellow scales.

0.3795 of the double salt gave 0.1165, or 30.69 % Pt.

0.2800 gave 0.0860 or 30.71 % Pt.

The formula $C_6H_{18}NCl \cdot PtCl_2$ requires 30.79 % of platinum.