

V. *On the Normal Paraffins.*—Part IV.By C. SCHORLEMMER, *F.R.S.*, and T. E. THORPE, *F.R.S.*

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IN the last communication made by one of us on this subject (Phil. Trans., 1880, p. 451), it was stated that we contemplated making a joint investigation on the heptane from *Pinus Sabiniana*. A large quantity of the pure heptane was treated with chlorine in the manner described in this series of communications (Phil. Trans., 1872, p. 111), and the chlorides boiling between 143° and $157^{\circ}\cdot 5$ were converted into the alcohols in the ordinary way. The primary alcohol boiled between 165° — 170° , whilst the secondary alcohol distilled over, for the most part, between 156° — 158° . The alcohols were then oxidised in the manner described in Phil. Trans., 1872, p. 121. The ketone obtained from the secondary alcohol was further oxidised by being heated with the chromic acid solution in sealed tubes at 100° . The liquid was then neutralised and the unattacked ketone was separated by distillation. In order to isolate the acids contained in the residue small quantities of sulphuric acid were added, and the acid which separated out (pentoic acid) was distilled off in a current of steam—the operation being repeated until the pentoic acid was no longer recognisable by its smell. The acetic acid contained in the residue was then separated by a further addition of sulphuric acid and distilled off by direct heating. The respective silver salts of the two acids were then prepared from the several fractions in the ordinary way. Analysis showed that the separation of the acids was complete.

I. SILVER salt from the normal alcohol.

(a) 0.4035 grm. salt gave 0.1842 grm. Ag = 45.6 per cent.

(b) 0.210 „ „ 0.0953 „ = 45.4 „

Calculated for silver heptoate 45.5 per cent.

II. SILVER salts from ketone from secondary alcohol.

0.2022 grm. salt A gave 0.1050 grm. Ag = 51.9 per cent.

0.1491 „ „ 0.0771 „ = 51.7 „

Silver pentoate = 51.6 Ag.

0.235 grm. salt B. gave 0.1518 grm. Ag = 64.59 per cent.

Silver acetate = 64.67 per cent.

The results of the oxidation show therefore that primary heptyl alcohol and methyl-pentyl-carbinol had been formed, as in the case of heptane from petroleum.

Another portion of the mixture of the monochlorides was then heated to 100° with alcoholic solution of potash, whereby in addition to heptylene a mixture of the ethyl heptyl ethers was obtained. The heptylene, purified by repeated rectification over sodium, boiled constantly at $98^{\circ}5$. It was placed in contact with an excess of fuming hydrochloric acid in the dark and in a well-closed bottle for six weeks. Heptylene from petroleum heptane was similarly treated.

Now it is remarkable that whilst hexylene from mannite combines completely with hydrochloric acid under these circumstances forming secondary hexyl chloride (Phil. Trans., 1880, p. 457), the greater part of the heptylene from *Pinus* heptane was found to be unattacked, not more than 10 per cent. of heptyl chloride having been formed. On the other hand, about one-half of the heptylene from petroleum had been converted into the chloride in accordance with the former observations made by one of us on this point.

The uncombined portions of both specimens of heptylene were again placed in contact with the fuming acid, and (the research being interrupted by other work) they were allowed so to remain for many months. At the expiration of this time it was found that the *Pinus* heptylene had united almost completely with the acid, whilst an additional quantity of the heptylene from petroleum had likewise entered into combination. It follows from this that, contrary to expectation, hydrochloric acid acting in the cold is not capable of effecting the separation of isomeric paraffins (Phil. Trans., 1880, p. 451).

It is remarkable that the *Pinus* heptylene should require so long a time to bring about its union with hydrochloric acid, since, as will be shown immediately, its constitution is exactly analogous to that of the hexylene from mannite or propyl-methyl ethylene, $C_3H_7.CH=CH.CH_3$, which so easily goes into combination.

In order to establish the constitution of the heptylene from *Pinus* it was oxidised by means of a solution of potassium dichromate in dilute sulphuric acid in the manner adopted by HECHT in the oxidation of hexylene from mannite (Ber. Deutsch. Chem. Ges., Bd. xi., S. 1152). The acids so formed were converted into the silver salts and analysed with the following results:—

Fraction.	Salt taken.	Silver found.	Silver pentoate 51·67.
1	0·0855	0·0443	51·81
2	0·0560	0·02875	51·34
3	0·1140	0·0590	51·75
4	0·1350	0·0700	51·84
5	0·0685	0·0350	51·09
6	0·1000	0·0540	54·00
7	0·2200	0·1370	62·27
8	0·1370	0·0855	64·60
9	0·1400	0·0910	65·00
			Silver acetate 64·67.

The first five fractions consisted of a fine crystalline powder, the last three were glistening needles.

These observations clearly indicate that only pentoic and acetic acids had been formed by the oxidation, and therefore that the *Pinus* heptylene is pure butyl-methyl-ethylene, $C_4H_9.CH=CH.CH_3$, which had been formed from the secondary heptyl chloride, $C_4H_9-CH_2-CHCl.CH_3$.

These results, taken in conjunction with those of former investigations, leave no doubt, therefore, that by the action of chlorine upon a normal paraffin not all the chlorides indicated by theory are formed, but only the primary and a secondary chloride which contains the group $-CHCl.CH_3$. One of us has formerly shown that by the action of bromine upon normal paraffins from petroleum only secondary bromides corresponding to chlorides are formed (Phil. Trans., 1878, Part I., p. 49). VENABLE has since shown that *Pinus* heptane is acted upon in the same way (Ber. Deutsch. Chem. Ges., Bd. xiii., S. 1649).