X.—On the Purification and Boiling Point of Methyl-hexyl Carbinol.

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THE boiling point of the octylic alcohol, methyl-hexyl carbinol, was found by its discoverer, Bouis, to be 180° , probably, however, uncorrected (*Compt. rend.*, xxxviii, 935, xli, 603), and by Chapman, when pure, to be 132° (*Journ. Chem. Soc.*, xviii, 290), whilst it was found by Schorlemmer to be 181° (*Proc. Roy. Soc.*, xvi, 376).

Lately Schorlemmer (*Journ. Chem. Soc.*, xxvii, 1029) has found, for an apparently pure alcohol, the boiling point 177° — 178° *, a result four degrees lower than the approximate determination by the author (*Journ. Chem. Soc.*, xxvii, 837).

The process by which the octylic alcohol employed by Schorlemmer was prepared is not stated; but it was purified by repeated treatment with acid sodium sulphite and fractional distillation, to remove the accompanying methyl-hexyl ketone, and the alcohol thus obtained boiled at 177° — 178° .

The very great persistency with which octylic alcohol retains traces of the ketone renders its purification a matter of great difficulty. Moreover, it was found that, although the method employed by Schorlemmer gave an apparently pure alcohol boiling at 177° — 179° , further examination showed that these means were not sufficient for the complete removal of the accompanying methyl-hexyl ketone, and that when this was removed by suitable processes, the purified alcohol boiled considerably higher.

The author has found that, even after all the ketone that is possible has been removed by fractional distillation and treatment with strong aqueous solution of acid sodium sulphite, an alcohol is obtained, boiling between 178° — 180° , though chiefly between 178° — 179° , but by the action of zinc chloride, which converts the octylic alcohol into octylene boiling at 125° — 126° , an appreciable amount of ketone can be separated, which is not removable by the former methods. Rectification over potassium hydrate exerts little influence beyond slightly raising the boiling point, the alcohol chiefly coming over at 179° .

When the method of purification of the crude alcohol adopted is to subject the alcohol to the action of potassium hydrate for some days at a moderate temperature, and then rectify it fractionally from the hydrate, the greater portion of the impurities is quickly removed. After repeating this treatment six or seven times, the alcohol reaches

* See the next Paper.

a condition similar to that already mentioned, is apparently unaffected by rectification over potassium hydrate, and usually boils for the most part at 178° — 179° , rising much higher towards the end.

When in this condition, however, the alcohol still retains traces of ketone; and on long standing at a gentle heat over potassium hydrate, turns slightly yellow: but even after being again rectified over the hydrate, which now removes most of the ketone, it still retains some, and boils between 178° — 180° . Further and longer treatment with potassium hydrate separates nearly all the remaining trace of ketone, the alcohol now generally boiling for the most part between 179° — 181° . Still longer treatment with the potassium hydrate for an additional period will generally remove the last trace, and after careful drying, the purified alcohol boils steadily at 181° , rising towards the end, however, above 182° .

Under certain conditions of preparation the crude oil contains a small quantity of octylene, and sometimes a very small amount of octane, which compounds being only very partially separated by the fractionation, lower throughout the boiling point of the alcohol very appreciably. To obtain the pure alcohol under these conditions, this olefine was removed by the action of bromine, which converts it into the heavy high-boiling octylene bromide, separable by washing with dilute potassium hydrate, and fractionating. When thus purified, the alcohol also boils chiefly at 181° , rising towards the end to above 182° .

The boiling points were throughout purposely determined with a single thermometer, with which the boiling point of water was constant at 100.2° , at 758 mm., but its examination at the end was prevented by fracture. Whenever, as was usual, the boiling point was too high to admit of the entire column of mercury being surrounded by the vapour, the results were carefully corrected by the use of Kopp's table. As these boiling points were not intended to be final determinations, as shown by the concluding paragraph, the results were given in the widest limits, and without reference to the atmospheric pressure, which, however, was high at the time. They seem, however, throughout to be usually somewhat higher than Professor Schorlemmer's.

Octylic alcohol, when pure, has a sp. gr. of 0.823 at 16° , and appears as a nearly colourless, very mobile, oily liquid, slightly yellowish, in very thick layers, with a decided peculiar odour, which, when a large surface is exposed to the air, as by being placed on paper, becomes very intense, aromatic, and persistent.

Oxygen has no action on the alcohol, even if transmitted through it when boiling, and the acid which Railton obtained by this means (*Journ. Chem. Soc.*, vi, 205) was probably the cœnanthylic acid formed by the distillation of the castor-oil soap without sufficient excess of

alkaline hydrate (*Journ. Chem. Soc.*, xxvii, 507). Nitric acid oxidises it violently, the chief products, besides nitro-butyric and other nitro-fatty acids, being nitro-octylene and dinitro-octylene. Permanganate of potassium and sulphuric acid convert it slowly into the corresponding ketone, methyl-hexyl ketone, whilst by the action of potassium bichromate and sulphuric acid, it is converted rapidly into methyl-hexyl ketone, and slowly into a mixture of acetic and caproic acids.

Bromine and iodine exert no action on the alcohol, but are readily dissolved; but in presence of phosphorus, they readily convert it into the corresponding bromide and iodide. Distilled with zinc chloride in presence of a current of hydrochloric acid gas, it is rapidly converted in octylic chloride, accompanied by a small quantity of octylene, while, if heated in a sealed tube with hydrochloric acid, it is less completely attacked. Distilled from fused zinc chloride, it is readily and completely converted into octylene, and likewise when heated with sulphuric acid it is converted principally into octylene, together, however, with some highly offensive-smelling bye-products.