

LXXVIII.—*The Bases contained in Scottish Shale Oil.*
Part II.

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THE examination of these bases has been continued, the fractions boiling between 164° and 180° being treated with mercuric chloride in much the same way as the fractions of lower boiling point (Trans., 1902, 81, 449); the results, however, have been disappointing, and although more than 400 grams of the mixed bases were examined, only two substances were isolated in a state of purity. Several of the less volatile bases form oily mercurichlorides, which solidify only after a long time, crystallisation being incomplete in some cases after an interval of several months; it is obviously impossible to obtain these substances reasonably pure even by repeated precipitation, whilst in other cases, where crystalline compounds were obtained, the very numerous recrystallisations which were needed caused great loss of material, and did not always result in the production of pure substances. Attempts were therefore made to effect a more perfect separation by using platinic chloride in place of the mercury salt, but without success; and the use of picric acid proved equally unsatisfactory.

2 : 4 : 6-Trimethylpyridine (*s*-Collidine).

2 : 4 : 6-Trimethylpyridine is by far the most abundant substance in these fractions, and as comparatively large quantities were obtained in a state of great purity, we were able to redetermine the boiling point and other constants given in our former communication; all these were confirmed, except that the boiling point as determined with a new short stem thermometer, certified at the Berlin Reichsan-

stalt, was found to be 171° (768 mm.) instead of 170.5° (763 mm.). On comparing two portions of the base, prepared from different fractions, a difference in boiling point of only 0.2° was found, showing that both specimens must have been very pure.

The aurichloride was easily obtained in long, yellow, hair-like crystals melting about 53° , and apparently containing one molecule of water of crystallisation; it is difficult to obtain an exact reading, however, for as soon as the crystals are dry they begin to effloresce, exposure to the air of the laboratory for a few hours rendering them quite anhydrous, the melting point rising to 112° . Many analyses were made of which the following are typical:

0.3244 lost 0.0110 at 95° , and yielded 0.1336 Au. $H_2O = 3.39$; Au (in the hydrated salt) = 41.2; (in the anhydrous) = 42.63.

0.3675 lost 0.0085 at 95° , and yielded 0.1530 Au.

$H_2O = 2.31$ per cent.; Au (in the hydrated salt) = 41.63; (in the anhydrous) = 42.62. $C_8H_{10}N, HAuCl_4, H_2O$ requires $H_2O = 3.76$ and Au = 41.18. In the anhydrous salt, Au = 42.74 per cent.

The aurichloride is soluble in about 40 parts of boiling, and in about 350 parts of cold water; the solution on boiling sometimes yields small quantities of a substance forming small, lemon-yellow needles, which are almost insoluble in water, and melt at about 178° . The conditions under which this salt is formed were not apparent, and attempts to prepare it in quantity failed, so that full analyses could not be made. There was no loss of weight on heating to 95° for two hours:

0.3486 gave 0.1614 Au. Au = 46.31.

0.4069 „ 0.1887 Au. Au = 46.12.

It is conceivable that this might be $C_8H_{10}N, AuCl_3$; (Au = 46.4) although no similar compounds have been observed in other cases.

2:3-Dimethylpyridine.

From the fraction boiling between 164° and 168° , about 25 grams of a mercurichloride were obtained in small, colourless needles melting somewhat indefinitely at 120° :

0.4074 gave 0.2753 HgS. Hg = 58.25.

$C_7H_9N, HCl, 2HgCl_2$ requires Hg = 58.4 per cent.

From this salt 2—3 grams of the base were obtained; it is a liquid lighter than, and insoluble in, water, having a pleasant, aromatic odour, and boiling at 163 — 164° (768 mm.). The platinichloride was

obtained very easily in orange-red crystals melting sharply and decomposing at 216° :

0.3490 gave 0.1084 Pt. $Pt = 31.07$.

$(C_7H_9N)_2, H_2PtCl_6$ requires $Pt = 31.24$ per cent.

The aurichloride formed yellow, straw-like crystals which melted at 96° , and decomposed slowly at about 225° ; the amount prepared was too small for a satisfactory analysis:

0.1410 gave 0.0618 Au. $Au = 43.83$.

$C_7H_9N, HAuCl_4$ requires $Au = 44.13$ per cent.

About $1\frac{1}{2}$ grams of the base were oxidised by potassium permanganate, the solution acidified with sulphuric acid, and silver nitrate added, when a gelatinous precipitate was obtained. After removing the silver by hydrogen sulphide, the product, being found to contain potassium, was dried on the water-bath, and boiled with absolute alcohol containing a little hydrochloric acid; the potassium chloride having been filtered off, the filtrate gave a fairly pure acid, which melted and decomposed at about 229° and gave a dirty white sublimate. A larger quantity of the acid was therefore heated in a very small test-tube to 250° , when a moderate amount of the sublimate was obtained, which after recrystallising from hot water melted at 229.5° ; the acid obtained by oxidation should therefore be quinolinic acid, and the sublimate, nicotinic acid. That the former was quinolinic acid was further proved by its giving a yellow colour with ferrous sulphate, and a fine green fluorescence with resorcinol; for comparison, some quinolinic acid was prepared by oxidising quinoline which had been synthesised by Skraup's reaction, and the two acids were found to agree in all respects. Since on oxidation the base is converted into pyridine-2:3-dicarboxylic acid, and is a lutidine, it can only be 2:3-dimethylpyridine, a compound which has not been hitherto described.

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